gular range $3.0° < 2\theta < 110°$, using Ni-filtered Cu K$\alpha$ radiation and the $2\theta/\theta$ mode. Least-squares refinement of the setting angles of 25 reflections with a good distribution throughout reciprocal space provided the unit cell dimensions: monoclinic, $a = 6.064$ (1) Å, $b = 10.427$ (2) Å, $c = 23.916$ (5) Å; $\beta = 91.10$ (1)°; $V = 1511.90$ Å$^3$; $F_{000} = 544$; $\mu$(Cu K$\alpha$) = 16.97 cm$^{-1}$; $Z = 4$; $D_{calcd} = 1.07$ g cm$^{-3}$. Systematic absences indicated the monoclinic space group $P_{21/c}$. Of 1907 independent reflections measured and corrected for Lorentz and polarization effects, 329 had intensities less than $3\sigma(F_o)$ and were not used in the refinement. The remaining 1578 reflections were used to solve and refine the structure.

Positions of all non-hydrogen atoms were located by using the direct-methods program available as part of the SHELXTL package.[12] Idealized hydrogen positions were calculated and tied to the associated non-hydrogen positions through a riding model. Final refinement of 16 non-hydrogen atoms using anisotropic thermal parameters and 28 hydrogen atoms using fixed isotropic thermal parameters, $U = 0.06$ Å$^2$, gave residual values of $R_1 = 0.0437$ and $R_2 = 0.0529$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = (\sigma^2F_o + gF_o^2)^{-1}$ and $g = 0.002$.

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**Registry No.** *cis*-**2**, 109181-88-6; *cis*-**4**, 123185-95-5; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; mesyl chloride, 124-63-0; *trans*-4-*tert*-butylcyclohexyl mesylate, 18508-90-2; 2-methyl-2-propanethiol, 75-66-1; *cis*-4-*tert*-butyl-1-(*tert*-butylthio)cyclohexane, 123185-94-4.

**Supplementary Material Available:** Listings of anisotropic thermal parameters for all non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms, bond distances, bond angles, torsional angles, and the fractional coordinates for *cis*-**2** and *cis*-**4** (12 pages). Ordering information is given on any current masthead page.

# Nucleophile and Nucleofuge Effects, Catalysis, and Stereochemistry in Vinylic Substitution of Electrophilic Nitro Olefins[1-3]

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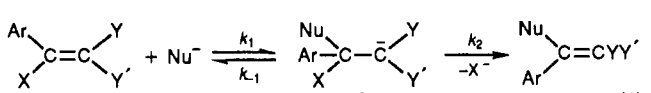
The substitution of (*E*)- and (*Z*)-β-iodo-α-nitrostilbenes (***E*-3-I** and ***Z*-3-I**) and of the (*E*)-β-chloro (***E*-3-Cl**) and of (*E*)-β-nitro (*E*-3-$NO_2$) analogues with several nucleophiles were studied in MeCN and EtOH. Amine catalysis in the substitution with morpholine and piperidine was observed in the reactions of ***E*-3-$NO_2$** in EtOH but not in MeCN. The reaction with $N_3^-$ gave 3,4-diphenylfuroxan. The reactions of ***E*-** and ***Z*-3-I** with *p*-TolS$^-$ in EtOH and NCS$^-$, piperidine, and morpholine in MeCN gave a single geometric isomer (presumably *E*) of the product, i.e., they show complete stereoconvergence. The precursor vinyl iodides were not isomerized during the substitution. $k_{E\text{-}3\text{-}Cl}/k_{E\text{-}3\text{-}I}$ values were 0.67–5.2 with the anionic nucleophiles and 20.1–23.7 with the amines. $k_{E\text{-}3\text{-}NO_2}/k_{E\text{-}3\text{-}Cl}$ were 2.8–9.8, and $k_{E\text{-}3\text{-}I}/k_{Z\text{-}3\text{-}I}$ were 1.86–2.86 (*p*-TolS$^-$, NCS$^-$) and 0.08–0.13 (piperidine, morpholine). $k_{Pip}/k_{Morp}$ ratios were 3.0–9.5. The relative nucleophilicity toward ***E*-3-Cl** changes by 4 orders of magnitude between the most reactive *p*-TolS$^-$ and the least reactive morpholine. The reaction is discussed in terms of a multistep substitution involving the intermediacy of zwitterions or carbanions. The lifetime of the carbanions is sufficiently long to enable a faster rotation around the $C_\alpha$–$C_\beta$ bond than nucleofuge expulsion. The lifetimes of the zwitterions derives from ***E*-3-$NO_2$** and amines are sufficiently long for deprotonation to compete with $NO_2$ expulsion in EtOH, but not in MeCN. The $k_{Cl}/k_I$ and $k_{NO_2}/k_{Cl}$ reactivity ratios are discussed in terms of a complex rate constant and contribution to the ratios from the individual rate constants. The $k_{E\text{-}3\text{-}I}/k_{Z\text{-}3\text{-}I}$ ratios were ascribed to different steric effects in the neutral precursors. Nucleophilicity scales toward electrophilic alkenes are discussed and the nitro group compared to other electron-withdrawing activators in vinylic substitution. The possibility of the intervention of other reaction routes is considered.

Our recent studies on nucleophilic vinylic reactions dealt mainly with substitution of highly activated electrophilic olefins (**1**) in a search for evidence that the substitution is a multistep process proceeding via the intermediacy of carbanions (**2**) or zwitterions (eq 1, shown for a negatively charged nucleophile).[4] The problem is that with good nucleofuges, e.g., Cl, Br, or $OSO_2R$, the lifetime of **2** is so short that nucleofuge expulsion is mostly faster than other reactions of **2**, making difficult its detection. For example, when X is a good nucleofuge, protonation of **2** is apparently slower than nucleofuge expulsion since Michael type adducts are not formed under the substitution conditions. Likewise, substitution is faster than $E \rightleftharpoons Z$ isomerization of the precursor alkene, except for a few systems.[5] On the other hand, the mild amine catalysis observed in the substitution of few ArC(X)=C(CN)$_2$, X = Cl, Br with




1 2 (1)

X = nucleofuge; Y, Y′ = electron-withdrawing groups

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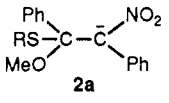
0022-3263/89/1954-5967$01.50/0 

anilines,[6] indicates that an intermediate zwitterion is deprotonated by another amine molecule in competition with nucleofuge expulsion. The main evidence for the intermediacy of **2** is stereochemical. Whereas with slightly or moderately activated systems the reaction usually proceeds with retention of configuration,[4] carbanion **2** formed in reactions of more electrophilic systems is sufficiently long-lived to allow competition of intramolecular rotation around the $C_\alpha$–$C_\beta$ bond with nucleofuge expulsion. This leads to a partial or complete stereoconvergence (i.e., formation of both *E* and *Z* substitution products starting from either the *E* or the Z precursor) for several systems.[1,2,4d,7]

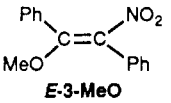
Other questions that we investigated in vinylic substitution include the relative reactivity of a few nucleophiles toward activated alkenes[8] or of a few nucleofuges on the same alkene.[6] We also discussed the effects of the β-activating groups on these parameters.[3,4a,d,6]

The nitro group has a well-recognized strong inductive and resonative electron-withdrawing function. This is shown by the $pK_a$ of nitromethane[9] as well as by the single kinetic study of nucleophilic substitution of a nitro-activated system.[10] However, the efficient negative charge delocalization shown in the fully developed α-nitro carbanions is not always reflected in the transition state for their formation.[11a,b]

The phenomena mentioned above can be connected with the kinetics of the carbanion formation or related to the properties of the fully developed carbanions. Hence, it was of interest to study the substitution of the (*E*)- and (*Z*)-β-iodo-α-nitrostilbenes (**3-I**) and of the (*E*)-β-chloro (**3-Cl**) and (*E*)-β-nitro (**3-$NO_2$**) analogues with nucleophiles, to search for amine catalysis in the substitution by amines, to investigate the possibility that $NO_2$ serves as a nucleofuge, and to determine the stereochemistry of the substitution of isomeric (*E*)- and (*Z*)-nitroalkenes. Two aspects of the reaction were discussed briefly in preliminary communications.[2,3] The reaction of *E*- and ***Z*-3-$NO_2$** with amines was investigated recently.[12] Evidence for the intermediacy of carbanion **2a** in the reaction of the α-methoxy analogue ***E*-3-$NO_2$** with thio nucleophiles was recently reported.[13]



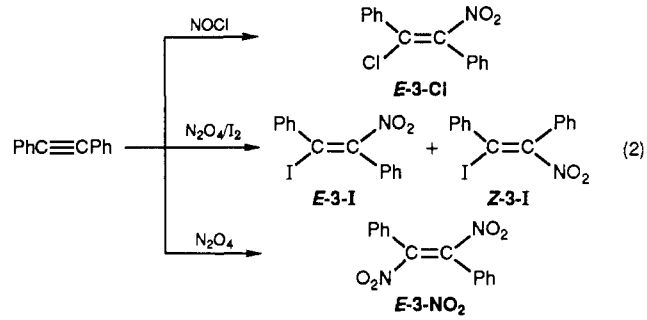

**2a**




***E*-3-MeO**

## Results

**Synthesis.** (*E*)-β-Chloro-α-nitrostilbene (***E*-3-Cl**) was prepared by the addition of nitrosyl chloride to diphenylacetylene according to Iwai et al.[14] Addition of iodine and nitrogen tetroxide to diphenylacetylene gave a mixture of (*E*)- and (*Z*)-β-iodo-α-nitrostilbenes (***E*-3-I** and ***Z*-3-I**)[15] which was separated by crystallization, whereas addition of nitrogen tetroxide alone gave a mixture of (*E*)- and (*Z*)-α,β-dinitrostilbenes from which the *E* isomer (***E*-3-$NO_2$**)[16] was separated (eq 2).

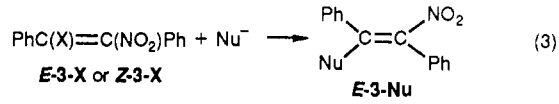



(2)

The configuration assignment of ***E*-3-I** and ***Z*-3-I** is based on the higher $\lambda_{max}$ in the UV spectra of the ***E*-3-I**.[17] We failed to corroborate the assignment by X-ray crystallography due to failure in obtaining good crystals.

**Reactions with Nucleophiles.** The kinetics of the reactions of ***E*-3-Cl** with seven nucleophiles in EtOH, with three nucleophiles in MeCN, and with *p*-$ClC_6H_4S^-$ and piperidine in MeOH was followed either at the $\lambda_{max}$ of the product or at a wavelength where the difference in absorption between ***E*-3-Cl** and the product ***E*-3-Nu** was appreciable. The substitution products ***E*-3-Nu** were isolated and identified by the usual analytical and spectroscopic methods (see the Experimental Section).

The reactions of ***E*-3-I** and ***Z*-3-I** with four nucleophiles in EtOH, and of ***E*-3-$NO_2$** with four nucleophiles in EtOH and MeCN were followed similarly (eq 3). Use of a high




(3)

X = Cl (*E* isomer): Nu = piperidine (Pip); morpholine (Morp); *p*-$YC_6H_4Z^-$ (Y = Cl, Me; Z = O, S), $NCS^-$

X = I (*E* and *Z* isomers): Nu = Pip, Morp, *p*-$MeC_6H_4S^-$, $NCS^-$

X = $NO_2$ (*E* isomer): Nu = Pip, Morp, $PhNH_2$, $NCS^-$

excess of the nucleophile ensured pseudo-first-order conditions in all the experiments. The high correlation coefficients ($r = 0.9999$) for all the first-order plots, coupled with the different reactivities of the two isomers, indicate the absence of an (*E*)-RX ⇌ (*Z*)-RX isomerization during any of these reactions. Constant second-order rate coefficients ($k_{obs}$) were obtained for all the cases (except for $N_3^-$, piperidine, and morpholine, see below) by dividing the pseudo-first-order constants by the nucleophile concentrations. The measured final optical densities always corresponded to the calculated value for a complete reaction, even in the reaction of ***Z*-3-I** with $NCS^-$ where only 41% of ***E*-3-SCN** was isolated under the synthetic conditions.

An *apparent* very mild amine catalysis was observed only in the reactions of piperidine and morpholine with ***E*-3-$NO_2$** in EtOH. $k_{obs}$ increased by 1.38- and 1.13-fold on 103- and 40-fold increase in [Pip] at 30 and 45 °C, respectively, and by 1.46- and 1.88-fold on 55- and 40-fold increase in [Morp] at 30 and 45 °C, respectively. The plots of $k_{obs}$ vs [amine] were nonlinear, with a relatively higher increase in $k_{obs}$ at the low amine concentrations. The

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**Table I. Kinetic Data for the Amine-Catalyzed Reactions with (*E*)-α,β-Dinitrostilbene in EtOH**

| amine | *T*, °C | $10^4$(slope),[a] $M^{-2}$ $s^{-1}$ | $10^3$(intercept),[a] $M^{-1}$ $s^{-1}$ | $k_3/k_2$[b] | *r*[c] |
|---|---|---|---|---|---|
| piperidine | 30 | 8.97 | 2.35 | 38.2 | 0.89 |
| morpholine | 30 | 3.00 | 0.698 | 49.2 | 0.98 |
| piperidine | 45 | 6.7 | 4.61 | 13.4 | 0.82 |
| morpholine | 45 | 9.11 | 0.911 | 10.0 | 0.89 |

[a] Parameters of the $k_{obs}$ vs [amine] plot. [b] Slope/intercept ratio. [c] Correlation coefficient of the linear $k_{obs}$ vs [amine] regression line.

**Table II. Second-Order Rate Coefficients for the Reaction of PhC(X)=C($NO_2$)Ph with Nucleophiles[a]**

| substrate | nucleophile | solvent | concn range, mol $L^{-1}$ | *n*[b] | $10^4k_2$, L $mol^{-1}$ $s^{-1}$ at 22 °C | 30 °C | 45 °C | $\Delta H^{\ddagger}$,[c] kcal $mol^{-1}$ | $\Delta S^{\ddagger}$ (303 K),[d] cal $mol^{-1}$ $K^{-1}$ | λ[e] nm |
|---|---|---|---|---|---|---|---|---|---|---|
| ***E*-3-Cl** | morpholine | EtOH | 0.338–1.521 | 4 | | 1.38 ± 0.11 | 3.32 ± 0.03 | 10.5 | −41.5 | 405 |
| ***E*-3-Cl** | piperidine | EtOH | 0.104–0.936 | 3 | | 4.41 ± 0.20 | 10.1 ± 0.2 | 9.9 | −41 | 408 |
| ***E*-3-Cl** | morpholine | MeCN | 0.069–1.69 | 5 | | 6.31 ± 0.11 | 12.5 ± 0.8 | 8.1 | −46.5 | 405 |
| ***E*-3-Cl** | piperidine | MeCN | 0.024–0.439 | 6 | | 50.2 ± 1.4 | 85.8 ± 2.9 | 6.2 | −48.5 | 408 |
| ***E*-3-Cl** | piperidine | MeOH | 0.10–0.9 | 5 | | 4.31 ± 0.05 | 10.3 ± 0.3 | 10.4 | −39.5 | 408 |
| ***E*-3-Cl** | $SCN^-$[g] | EtOH | 0.09–0.263 | 3 | | 1.91 ± 0.06 | 4.47 ± 0.02 | 10.1 | −42 | 318 |
| ***E*-3-Cl** | $SCN^-$[g] | MeCN | 0.076–0.332 | 4 | | 2.49 ± 0.05 | 7.58 ± 0.20 | 13.5 | −30.5 | 318 |
| ***E*-3-Cl** | *p*-$MeC_6H_4S^-$[f] | EtOH | 0.00112–0.003 | 4 | 32700 ± 2300 | 60200 ± 5000 | | 10.1 | −21.5 | 350 |
| ***E*-3-Cl** | *p*-$ClC_6H_4S^-$[f] | EtOH | 0.0014–0.006 | 4 | 17500 ± 700 | 26000 ± 1200 | | 8.2 | −29.5 | 350 |
| ***E*-3-Cl** | *p*-$ClC_6H_4S^-$[f] | MeOH | 0.0013–0.0039 | 3 | 7830 ± 140 | 12300 ± 400 | | 9.5 | −22.2 | 350 |
| ***E*-3-Cl** | *p*-$MeC_6H_4O^-$[f] | EtOH | 0.027–0.291 | 4 | | 27.7 ± 1.8 | 85.2 ± 3.1 | 13.7 | −24.9 | 363 |
| ***E*-3-Cl** | *p*-$ClC_6H_4O^-$[f] | EtOH | 0.030–0.238 | 4 | | 10.0 ± 0.2 | 35.6 ± 0.9 | 15.5 | −21 | 363 |
| ***E*-3-Cl** | $N_3^-$[g] | MeOH | 0.034–0.135 | 3 | | 52.1 ± 0.9 | 156 ± 10 | 13.3 | −25 | 270 |
| ***E*-3-Cl** | $N_3^-$[g] | 80% dioxan–20% $H_2O$ | 0.021–0.063 | 3 | | 101.5 ± 1.5 | 340 ± 3.8 | 14.7 | −18.9 | 270 |
| ***E*-3-I** | morpholine | EtOH | 0.412–0.824 | 3 | | 0.050 ± 0.009 | 0.163 ± 0.004 | 12.4 | −41.5 | 405 |
| ***Z*-3-I** | morpholine | EtOH | 0.206–0.896 | 7 | | 0.487 ± 0.005 | 1.27 ± 0.03 | 11.5 | −40 | 405 |
| ***E*-3-I** | piperidine | EtOH | 0.10–0.9 | 5 | | 0.192 ± 0.008 | 0.504 ± 0.018 | 11.6 | −41.5 | 408 |
| ***Z*-3-I** | piperidine | EtOH | 0.202–0.808 | 5 | | 2.36 ± 0.10 | 5.81 ± 0.17 | 10.8 | −39.3 | 408 |
| ***E*-3-I** | *p*-$MeC_6H_4S^-$[f] | EtOH | 0.0012–0.0078 | 4 | 10500 ± 700 | 16700 ± 700 | | 9.7 | −25.1 | 350 |
| ***E*-3-I** | *p*-$MeC_6H_4S^-$[f] | EtOH | 0.0012–0.0048 | 4 | 3810 ± 10 | 5830 ± 80 | | 8.8 | −30.4 | 350 |
| ***E*-3-I** | $N_3^-$[g] | MeOH | 0.0375–0.1125 | 3 | | 78.1 ± 0.6 | 125 ± 4 | 5.4 | −50.5 | 287 |
| ***E*-3-I** | $N_3^-$[g] | 80% dioxan–20% $H_2O$ | 0.0375–0.06 | 3 | | 66.0 ± 0.4 | 112 ± 3 | 6.1 | −48.5 | 287 |
| ***E*-3-I** | $SCN^-$[g] | EtOH | 0.0428–0.167 | 3 | | 0.37 ± 0.01 | 1.05 ± 0.06 | 12.7 | −37.2 | 318 |
| ***Z*-3-I** | $SCN^-$[g] | EtOH | 0.0454–0.182 | 3 | | 0.147 ± 0.001 | 0.564 ± 0.004 | 16.3 | −27.3 | 318 |
| ***E*-3-$NO_2$** | morpholine | MeCN | 0.00976–0.195 | 6 | | 69.3 ± 0.3 | 134 ± 7 | 7.9 | −42.5 | 405 |
| ***E*-3-$NO_2$** | piperidine | MeCN | 0.00128–0.077 | 7 | | 656 ± 20 | 907 ± 28 | 3.5 | −53 | 408 |
| ***E*-3-$NO_2$** | morpholine | EtOH | 0.0368–1.017 | 7 | | 6.98 ± 0.1 | 9.11 ± 0.7 | 2.8 | −63.5 | 405 |
| ***E*-3-$NO_2$** | piperidine | EtOH | 0.0317–0.816 | 7 | | 23.5 ± 0.8 | 46.1 ± 0.8 | 7.9 | −44.5 | 408 |
| ***E*-3-$NO_2$** | $SCN^-$[g] | EtOH | 0.0227–0.204 | 4 | | 18.6 ± 0.8 | 42.9 ± 0.9 | 10.0 | −38.2 | 318 |
| ***E*-3-$NO_2$** | $C_6H_5NH_2$ | EtOH | 0.02–0.8 | 6 | | 7.53 ± 0.28 | 14.0 ± 0.2 | 7.3 | −48.8 | 400 |

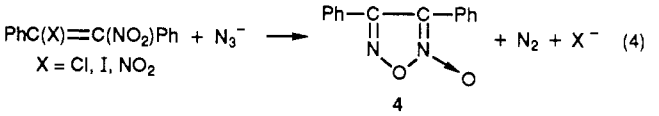
[a] [3-X] = $(9 \times 10^{-5})$–$(1.6 \times 10^{-3})$. [b] Number of nucleophilic concentrations used. [c] ±1 kcal $mol^{-1}$. [d] ±3 cal $mol^{-1}$ $K^{-1}$. [e] Wavelength of the kinetic measurement. [f] Sodium salt. [g] Potassium salt.

nonlinearity is reflected by the correlation coefficients of 0.82–0.98 calculated for the linear plots. The kinetic data for the amine-catalyzed reactions of ***E*-3-$NO_2$** are given in Table I. Catalysis for the same reactions in MeCN was not observed.

The reactions of the $ArS^-$ and $ArO^-$ ions were conducted by using the thiol or the phenol with excess of NaOEt in EtOH. When excess of base was not used with the ArSH, the rate coefficients were lower, indicating incomplete ionization to the thiolate ion.

The kinetic data and the derived activation parameters are given in Table II. Table III demonstrates the catalysis observed for ***E*-3-$NO_2$** with piperidine and morpholine in EtOH and its absence in MeCN, the dependence of $k_{obs}$ on the concentration of NaOEt in the reactions of *p*-$MeC_6H_4SH$ and the first-order kinetics for the reaction of ***E*-3-$NO_2$** with $N_3^-$ in MeOH. The chloride/iodide ($k_{E\text{-}3\text{-}Cl}/k_{E\text{-}3\text{-}I}$), the nitro/chloride ($k_{E\text{-}3\text{-}NO_2}/k_{E\text{-}3\text{-}Cl}$) and the *E* to *Z* iodide ($k_{E\text{-}3\text{-}I}/k_{Z\text{-}3\text{-}I}$) reactivity ratios for the different nucleophiles are given in Table IV. Table V gives the piperidine/morpholine ratios under various conditions and two $k_{Morp}/k_{PhNH_2}$ ratios with ***E*-3-$NO_2$**. Relative nucleophilicities toward ***E*-3-X** are given in Table VI.

The reactions of $NaN_3$ with ***E*-3-Cl** and ***E*-3-I** in MeOH or in 80% aqueous dioxane, or with ***E*-3-$NO_2$** in MeOH were followed at their $\lambda_{max}$ and gave the known 3,4-diphenylfuroxan (**4**)[18] (eq 4). The former reactions were

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overall second-order, first-order in both **3** and $N_3^-$, while the reaction with ***E*-3-$NO_2$** was first-order in the substrate, and independent of $[N_3^-]$ at the concentration range of $(5.6–44.8) \times 10^{-3}$ $M^{-1}$ (Table III).

**Stereochemistry of the Substitution.** The stereochemistry of the reactions of ***E*-** and ***Z*-3-I** with *p*-$MeC_6H_4S^-$ in EtOH, and $NCS^-$ and $N_3^-$ in MeOH was investigated. Both isomers gave the same product with each nucleophile (Table VII).[2] Chromatography of the crude reaction mixtures on silica never showed even traces of the geometrical isomers. The isolated yields (Table VII) are therefore lower limits for the stereochemical purity. It is difficult to assign unequivocally the products' configuration with *p*-$MeC_6H_4S^-$ and $CNS^-$ from their spectral data, and the less strained *E* configuration is tentatively

(18) Emmons, W. D.; Freeman, J. P. *J. Org. Chem.* **1957**, *22*, 456.

**Table III. Examples of Reactions of PhC(X)=C($NO_2$)Ph with Nucleophiles**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (a) ***Z*-3-I** + *p*-$MeC_6H_4S^-$ in EtOH | | | | | | | | | | | | | | |
| $10^3$[$EtO^-$], M | 1.96 | 2.94 | 3.92 | 3.92 | 5.20 | 5.88 | 7.80 | 10.4 | | | | | | |
| $10^3$[*p*-$MeC_6H_4SH$], M | 1.2 | 1.8 | 1.8 | 2.4 | 2.4 | 3.6 | 3.6 | 4.8 | | | | | | |
| $10^2k_{obs}$, $M^{-1}$ $s^{-1}$ at 22 °C | | | 38.0 | | 37.6 | | 37.0 | 39.8 | | | | | | |
| $10^2k_{obs}$, $M^{-1}$ $s^{-1}$ at 30 °C | 57.5 | 59.0 | | 57.0 | | 59.5 | | | | | | | | |
| (b) ***E*-3-Cl** + *p*-$MeC_6H_4S^-$ in EtOH | | | | | | | | | | | | | | |
| $10^3$[$EtO^-$], M | 0.99 | 1.32 | 1.98 | 2.64 | 2.16 | 2.88 | 4.33 | 5.76 | | | | | | |
| $10^3$[*p*-$MeC_6H_4SH$], M | 0.99 | 1.32 | 1.98 | 2.64 | 1.13 | 1.50 | 2.25 | 3.00 | | | | | | |
| $k_{obs}$, $M^{-1}$ $s^{-1}$ at 30 °C | 4.64 | 4.78 | 5.74 | 5.44 | 6.10 | 6.00 | 6.05 | 5.95 | | | | | | |
| (c) ***E*-3-$NO_2$** + piperidine in EtOH | | | | | | | | | | | | | | |
| $10^2$[piperidine], M | 0.79 | 1.58 | 1.78 | 3.17 | 3.56 | 8.9 | 10.2 | 17.8 | 20.4 | 40.8 | 71.2 | 81.6 | | |
| $10^3k_{obs}$, $M^{-1}$ $s^{-1}$ at 30 °C | 2.18 | 2.31 | | 2.43 | | | 2.50 | | 2.75 | 2.78 | | 3.00 | | |
| $10^3k_{obs}$, $M^{-1}$ $s^{-1}$ at 45 °C | | | 4.44 | | 4.64 | 4.74 | | 4.86 | | | 5.01 | | | |
| (d) ***E*-3-$NO_2$** + morpholine in EtOH | | | | | | | | | | | | | | |
| $10^2$[morpholine], M | 1.79 | 1.84 | 3.58 | 3.68 | 7.16 | 11.3 | 17.9 | 22.6 | 35.8 | 45.2 | 53.7 | 67.8 | 71.6 | 101.7 |
| $10^4k_{obs}$, $M^{-1}$ $s^{-1}$ at 30 °C | | 6.75 | | 7.10 | | 7.50 | | 7.60 | | 8.54 | | 9.15 | | 9.85 |
| $10^4k_{obs}$, $M^{-1}$ $s^{-1}$ at 45 °C | 8.05 | | 8.56 | | 9.75 | | 13.1 | | 13.2 | | 13.5 | | 15.1 | |
| (e) ***E*-3-$NO_2$** + piperidine in MeCN | | | | | | | | | | | | | | |
| $10^3$[piperidine], M | 1.29 | 2.57 | 5.14 | 6.63 | 8.84 | 10.28 | 13.26 | 22.1 | 25.7 | 44.2 | 51.4 | 77.1 | 88.4 | |
| $10^2k_{obs}$, $M^{-1}$ $s^{-1}$ at 30 °C | 6.35 | 6.80 | 6.90 | 7.09 | 6.70 | 6.69 | 6.70 | 7.32 | 6.47 | 7.0 | 6.40 | 6.32 | 6.95 | |
| $10^2k_{obs}$, $M^{-1}$ $s^{-1}$ at 45 °C | | 9.20 | 8.65 | | | 9.35 | | | | | | | | |
| (f) ***E*-3-$NO_2$** + $N_3^-$ in MeOH | | | | | | | | | | | | | | |
| $10^2[N_3^-]$, M | 0.54 | 1.12 | 2.24 | 3.36 | 4.48 | | | | | | | | | |
| $10^3k_1$, $s^{-1}$ at 30 °C | | 1.54 | 1.41 | 1.46 | 1.61 | | | | | | | | | |
| $10^3k_1$, $s^{-1}$ at 45 °C | 2.23 | 2.93 | 3.16 | 3.75 | | | | | | | | | | |

**Table IV. Nucleofuge and Geometry Effects in the Reaction of Compounds 3, PhC(X)=C($NO_2$)Ph (X = Cl, I, $NO_2$), with Nucleophiles**

| nucleophile | *T*, °C | solvent | $k_{E\text{-}3\text{-}Cl}/k_{E\text{-}3\text{-}I}$ | $k_{E\text{-}3\text{-}NO_2}/k_{E\text{-}3\text{-}Cl}$ | $k_{E\text{-}3\text{-}I}/k_{Z\text{-}3\text{-}I}$ |
|---|---|---|---|---|---|
| *p*-$MeC_6H_4S^-$ | 30 | EtOH | 3.60 | | 2.86 |
| *p*-$MeC_6H_4S^-$ | 22 | EtOH | 3.54 | | 2.75 |
| $SCN^-$ | 30 | EtOH | 5.2 | 9.8 | 2.52 |
| $SCN^-$ | 45 | EtOH | 4.3 | 9.6 | 1.86 |
| $N_3^-$ | 30 | MeOH | 0.67 | | |
| $N_3^-$ | 30 | 80% dioxan–20% $H_2O$ | 1.54 | | |
| $N_3^-$ | 45 | MeOH | 1.25 | | |
| $N_3^-$ | 45 | 80% dioxan–20% $H_2O$ | 2.95 | | |
| piperidine | 30 | EtOH | 23.0 | 5.3 | 0.081 |
| piperidine | 45 | EtOH | 20.1 | 4.5 | 0.087 |
| morpholine | 30 | EtOH | 23.7 | 5.1 | 0.12 |
| morpholine | 45 | EtOH | 20.4 | 2.8 | 0.128 |

**Table V. Reactivity Ratios of Amines with PhC(X)=C($NO_2$)Ph, X=Cl, I, $NO_2$**

| compound | *T*, °C | solvent | $k_{Pip}/k_{Morp}$ | $k_{Morp}/k_{PhNH_2}$ |
|---|---|---|---|---|
| ***E*-3-Cl** | 30 | EtOH | 3.2 | |
| ***E*-3-Cl** | 45 | EtOH | 3.04 | |
| ***E*-3-Cl** | 30 | MeCN | 7.95 | |
| ***E*-3-Cl** | 45 | MeCN | 6.86 | |
| ***E*-3-I** | 30 | EtOH | 3.30 | |
| ***E*-3-I** | 45 | EtOH | 3.15 | |
| ***Z*-3-I** | 30 | EtOH | 4.86 | |
| ***Z*-3-I** | 45 | EtOH | 4.58 | |
| ***E*-3-$NO_2$** | 30 | EtOH | 3.16 | 0.93 |
| ***E*-3-$NO_2$** | 45 | EtOH | 5.05 | 0.65 |
| ***E*-3-$NO_2$** | 30 | MeCN | 9.5 | |
| ***E*-3-$NO_2$** | 45 | MeCN | 6.77 | |

proposed. Only **4** was isolated from the reaction with $N_3^-$, probably by cyclization of the initially formed vinylic azide.

The identity of the products obtained from ***E*-3-I** and ***Z*-3-I** was established by mixed melting point, and by the identical IR spectra and retention times in TLC on silica (eluent: 10% acetone–90% petroleum ether). The main product from the reaction of $NCS^-$ with ***Z*-3-I** was the vinylic thiocyanate **3-SCN**, but a second product, which lacks a SCN absorption at the 2100-$cm^{-1}$ region, was isolated in 20% yield but was not investigated further.

**Table VI. Relative Nucleophilicity ($k_{obs}$, $M^{-1}$ $s^{-1}$) toward PhC(X)=C($NO_2$)Ph in EtOH at 30 °C**

| | substrate | | | |
|---|---|---|---|---|
| nucleophile | ***E*-3-Cl** | ***E*-3-I** | ***E*-3-$NO_2$** | ***E*-3-H**[b] |
| $EtS^-$ | | | | 3795 |
| *p*-$MeC_6H_4S^-$ | 43600 | 287000 | | |
| *p*-$ClC_6H_4S^-$ | 18800 | | | |
| *p*-$MeC_6H_4O^-$ | 20.1 | | | |
| *p*-$ClC_6H_4O^-$ | 7.25 | | | |
| piperidine | 3.20 | 3.30 | 3.40 | 6.6 |
| $SCN^-$ | 1.38 | 6.40 | 2.70 | |
| morpholine | 1.00 | 1.00 | 1.00 | 1.0 |
| aniline | | | 1.08 | |
| $N_3^-$ | 37.8[a] | 1562[a] | | |

[a] Reaction of $N_3^-$ in MeOH as solvent. [b] From ref 30; in 50% DMSO–50% $H_2O$ at 20 °C.

The reactions of piperidine and morpholine gave the same enamine starting from either ***E*-3-I** or ***Z*-3-I**. TLC analysis of the reaction mixtures did not show even traces of an isomeric enamine. We tentatively suggested an *E* configuration for the enamines for steric reasons[2] (see below).

**Search for Isomerization of the Starting Iodides or the *E* Products.** ***Z*-3-I** is less stable than ***E*-3-I** as shown by its complete conversion to ***E*-3-I** on standing with one crystal of iodine in EtOH for 1 week at room temperature. When 1 equiv of ***Z*-3-I** was reacted with 0.5 equiv of *p*-$MeC_6H_4S^-$ in EtOH, the NMR spectrum of the crude mixture after a normal workup showed only the multiplet of the product at δ 6.69–6.90 and the signal of ***Z*-3-I** at δ 7.47 ppm, but not the signal at δ 7.73 of ***E*-3-I**. A ***Z*-3-I** → ***E*-3-I** isomerization is therefore excluded.

In an attempt to obtain ***Z*-3-$SC_6H_4Me$-*p*** and ***Z*-3-SCN**, the corresponding *E* isomers were irradiated for 8 h in MeOH and $CCl_4$ under nitrogen, but no trace of the *Z* isomers was detected.

## Discussion

New aspects of vinylic substitution of the present work involve the determination of a short nucleophilicity scale toward the highly activated system and its comparison with scales toward less activated systems, the observation

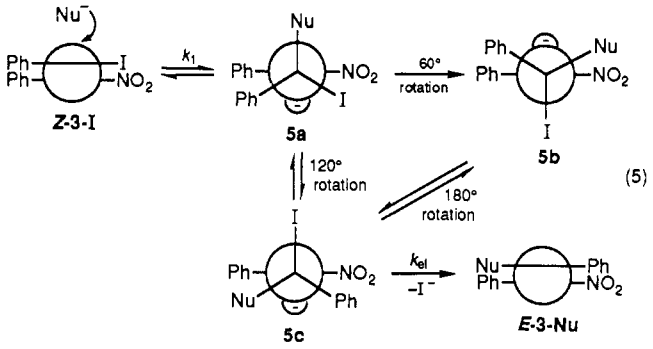
**Table VII. Stereochemistry of the Substitution of PhC(I)=C($NO_2$)Ph by Nucleophiles**

| substrate | nucleophile[a] | solvent | reaction time, h | T, °C | product[c] |
|---|---|---|---|---|---|
| ***E*-3-I** | *p*-$MeC_6H_4S^-$[b] | EtOH | 1 | 25 | >93% ***E*-3-$SC_6H_4Me$-*p*** |
| ***Z*-3-I** | *p*-$MeC_6H_4S^-$[b] | EtOH | 1 | 25 | >91% ***E*-3-$SC_6H_4Me$-*p*** |
| ***E*-3-I** | $SCN^-$ | MeCN | 96 | 25 | >89% ***E*-3-SCN** |
| ***Z*-3-I** | $SCN^-$ | MeCN | 168 | 25 | >41% ***E*-3-SCN** |
| ***E*-3-I** | $N_3^-$ | MeOH | 24 | 0 | >78% **4** |
| ***Z*-3-I** | $N_3^-$ | MeOH | 24 | 0 | >75% **4** |
| ***E*-3-I** | piperidine | MeCN | 2 | 25 | 90% ***E*-3-Pip** |
| ***Z*-3-I** | piperidine | MeCN | 2 | 25 | 90% ***E*-3-Pip** |
| ***E*-3-I** | morpholine | MeCN | 12 | 25 | 90% ***E*-3-Morp** |
| ***Z*-3-I** | morpholine | MeCN | 12 | 25 | 90% ***E*-3-Morp** |
| ***E*-3-I** | $MeO^-$[d] | MeOH | 140 | rt[f] | 7:3 ***Z*-3-OMe:*E*-3-OMe**[e] |

[a] [Nu]/[3] = 10 except when otherwise stated. [b] [Nu]/[3] = 1. [c] Yield of the isolated product. The assignment is tentative (see text). [d] [Nu]/[3] = 1.54. [e] Reference 7b. [f] rt = room temperature.

of amine catalysis, quantitative data on reaction with other nucleophiles in a system carrying a nitro nucleofuge, and the stereochemistry of the substitution of a nitro-activated system. Extensions of previous data include the vinyl iodide vs vinyl chloride reactivity and the ***E*-3-I/*Z*-3-I** reactivity ratio.

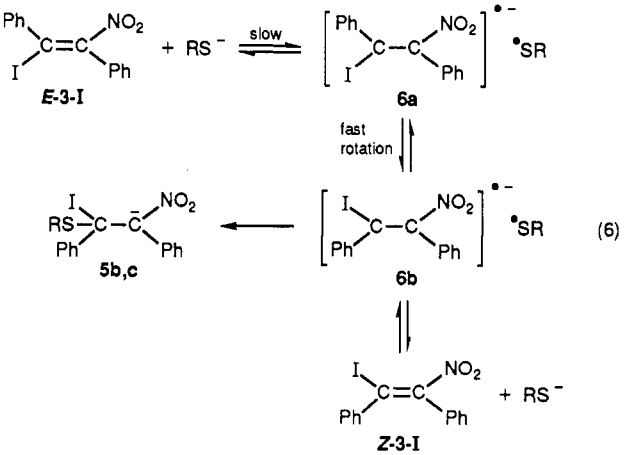
**Stereochemistry of the Substitution.** The main stereochemical feature is the formation of the same single substitution product starting from either ***E*-3-I** or ***Z*-3-I** in each of the reactions of three anionic nucleophiles which cover an appreciable reactivity difference. The formation of an identical mixture of geometrical isomers of the products from both isomeric precursors is regarded mechanistically as "complete stereoconvergence".[4,7] We have shown that partial or nearly complete stereoconvergence is the stereochemical outcome of the substitution of many activated systems.[7,19] Since the stereochemistry was discussed briefly earlier[2] it is sufficient to note that in terms of eq 5 complete stereoconvergence means that intramolecular rotation ($k_{rot}$) which equilibrates the carbanionic conformers **5b** and **5c** is faster than $I^-$ expulsion ($k_{el}$).[5,20]




(5)

The stereochemistry of the products is presented in eq 5 as ***E*-3-Nu**. It is not unequivocally proven but tentatively inferred from the UV data. Fortunately, the actual stereochemistry of the product does not affect the mechanistic conclusion. The intermediacy of relatively long lived carbanions is based on the operation of the Curtin–Hammett principle[21] as applied to product formation from only one carbanionic conformer, presumably **5c**, rather than on the stereochemistry of the product.

However, other substitution routes leading to stereoconvergence should be considered. A likely route, initiated by a single-electron transfer (SET) is depicted in eq 6.




(6)

The α-nitrobenzylic system of **3** and a soft thio nucleophile are a classic combination for this route.[22] The importance of such process is emphasized by works of Pross and Shaik[23] and its likely operation in nucleophilic additions to electrophilic nitro olefins can be deduced from the work of Hoz.[23b-e] If eq 6 in which **5a** (or **5b** or **5c**) is formed by two consecutive SET's is followed, and the anion radical **6a** formed from ***E*-3-I** undergoes internal rotation to **6b** before recombination with the RS•, a **5b/5c** mixture will be formed, and arguments related to the lifetime of carbanion **5** become irrelevant. Certain alkenes isomerize by a similar mechanism.[24] The absence of isomerization of ***Z*-3-I** in the reaction with 0.5 equiv of *p*-$MeC_6H_4S^-$, which

(19) (a) For earlier examples of partial or complete stereoconvergence, arising from the intermediate formation of long-lived carbanions carrying poor nucleofuges X, see the following. X = F: Marchese, G.; Naso, F.; Modena, G. *J. Chem. Soc. B* **1969**, 290. Marchese, G.; Modena, G. *Chimica et Industria* **1971**, *53*, 760. X = $NO_2$: ref 18. For postisomerization when X = Cl, see: Aguiar, A. M.; Archibald, T. G.; Kapicak, L. A. *Tetrahedron Lett.* **1967**, *45*, 4447. Landini, D.; Modena, G.; Montanari, F.; Naso, F. *J. Chem. Soc. B* **1969**, 243. (b) The formation of only one product in the substitution of (*E*)-PhC(Cl)=$CHNO_2$ by $NCS^-$[14] may also involve formation of a long-lived carbanion, although a preisomerization of the chloro olefin is also a possibility with this nucleophile.

(20) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095. (b) Apeloig, Y.; Karni, M.; Rappoport, Z. *Ibid.* **1983**, *105*, 2784.

(21) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

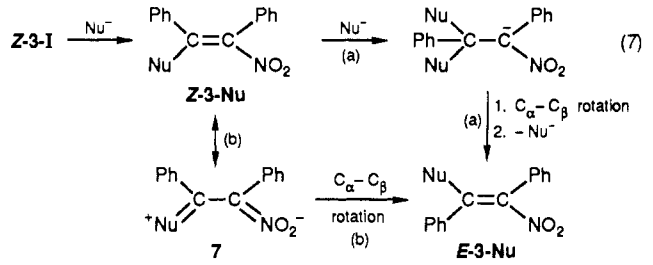
(22) For reviews, see: (a) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (b) Kornblum, N. In *The Chemistry of the Functional Groups, Supplement F*; Patai, S., Ed.; Wiley: New York, 1982; Chapter 10, pp 361–393. For a recent paper see: Kornblum, N.; Cheng, L.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Kestner, M. M.; Manthey, J. W.; Musser, M. T.; Pinnick, H. W.; Snow, D. H.; Stuchal, F. W.; Swiger, R. T. *J. Org. Chem.* **1987**, *52*, 196.

(23) (a) For reviews, see: Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. Pross, A. *Ibid.* **1985**, *18*, 212. (b) Hoz, S.; Spiezman, D. *J. Org. Chem.* **1983**, *48*, 2904. (c) Hoz, S. *Ibid.* **1982**, *47*, 3545. (d) Hoz, S. *Adv. Chem. Ser.* **1987**, *215*, 181. (e) Gross, Z.; Hoz, S. *J. Am. Chem. Soc.* **1988**, *110*, 7489.

(24) (a) Chien, C. K.; Wang, H. C.; Szwarc, M.; Bard, A. J.; Itaya, K. *J. Am. Chem. Soc.* **1980**, *102*, 3100 and reference 3 therein to the work of Szwarc's group. (b) Todres, Z. V. *Russ. J. Phys. Chem.* **1980**, *54*, 1097. (c) Todres, Z. V.; Kursanov, D. N. *Dokl. Akad. Nauk USSR* **1972**, *205*, 1117. (d) Dyusengaliev, K. I.; Borisov, Y. A.; Todres, Z. V. *Izv. Akad. Nauk SSSR* **1981**, 1159. (e) For a review, see: Todres, Z. V. *Tetrahedron* **1987**, *17*, 3839. (f) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; p 192.

is corroborated by the excellent pseudo-first-order plots, can be interpreted in two ways. Either reaction via eq 5 rather than via eq 6 takes place or starting from ***Z*-3-I** in eq 6 the **6b** → **5a** process is faster than the **6b** → ***E*-3-I** route. Rotation around the $C_\alpha$–$C_\beta$ bond in the anion radical can have a considerable barrier,[24a,e] so that if the radical–radical ion recombination **6a** → **5c** is faster than the **6a** → **6b** rotation, the stereochemical arguments for the route of eq 5 remain valid.

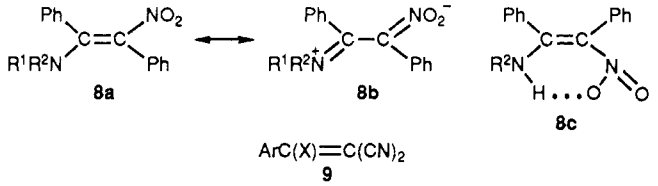
Other mechanisms involve postisomerization of the initial products by excess nucleophile (eq 7a) or product isomerization by a thermal rotation around the partial single $C_\alpha$–$C_\beta$ bond of **3-Nu** (cf. 7) due to the complementary push (RS) and pull ($NO_2$) substituents (eq 7b). Both




(7)

routes were rejected for other systems which undergo partial stereoconvergence.[7] However, they cannot be unequivocally excluded since the rotations may be faster in compounds **3** due to a greater negative charge dispersal by the $NO_2$ group.

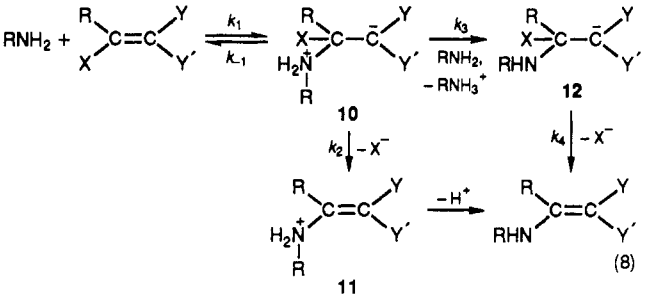
The complete stereoconvergence obtained in the substitutions of ***E*-3-I** and ***Z*-3-I** with piperidine and morpholine do not indicate product formation from a long-lived zwitterion since enamines **8** are configurationally unstable due to the single-bond character of the $C_\alpha$–$C_\beta$ bond (cf. hybrid **8b**).[25,26]




The evidence for an intramolecular hydrogen bonding between the amino and the nitro groups (cf. **8c**) suggests a *Z* structure for several nitro enamines when $R^1$ = H.[27] Hence, this is probably the structure of the anilino enamine. The similarity in the spectral properties of enamines when $R^1$ = H and $R^1 \neq$ H suggest *Z* structures also when $R^1 \neq$ H.[27] The $\epsilon$ values in the UV spectra of the piperidino and morpholino enamines are lower than those of the related enamines[27] whereas the NMR signals are in approximately the same positions of enamines with $R^1$ = $R^2$ = H. Consequently, the analogy is not compelling in the absence of data for the other isomer and we still prefer an *E* structure on steric grounds.

In sum, in the absence of evidence to the contrary we will analyze the reaction in terms of the conventional eq 5.

**Amine Catalysis in the Substitution of *E*-3-$NO_2$.** Amine catalysis in vinylic substitution was observed for systems substituted by poor nucleofuges (e.g., F, OR, CN),[28] but weak amine catalysis was found only in the substitution of compounds **9** with the good nucleofuges X = Cl or Br by amines.[6] Base catalysis is observed when nucleofuge expulsion from the ammonium moiety of the initially formed zwitterion **10** to give **11** ($k_2$) becomes slower than deprotonation ($k_3$) of **10** to **12** by another amine molecule (eq 8). In this case eq 9 applies where $k_{obs}$ is the second-order rate constant and $k_3/k_2$ is the catalyzed to the noncatalyzed rate constant ratio.

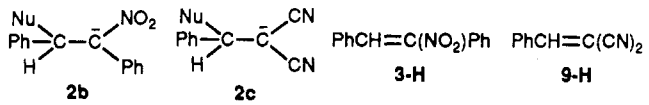



(8)

$$k_{obs} = k_1(k_2 + k_3[\text{amine}])/(k_{-1} + k_2 + k_3[\text{amine}]) \quad (9)$$

Increased electron withdrawal by Y and Y′ increases the acidity of the ammonium ion moiety in **10** with a consequent increase in $k_3$ and decreases $k_2$, the expulsion rate of $X^-$. Hence, it is predicted that the approximately similar resonative electron-withdrawal ability of $NO_2$ compared with two CN groups (based on $pK_a$'s in water[9a]) may result in amine catalysis for ***E*-3-Cl**, ***E*-3-I**, and ***Z*-3-I**. This is supported by extensive amine and base catalysis in the substitution of the structurally analogous 1,2-dinitrobenzene by piperidine[29] and aliphatic primary amines.[29b] As found for systems **9**[28] the catalysis should be more pronounced in the aprotic MeCN than in the protic EtOH which can replace the amine in the deprotonation of **10**.

That $k_{-1}$ and $k_2$ from **10** (and $k_4$ from **12**) are much larger for **9**, X = Cl, than for ***E*-3-Cl** can be deduced from the $k_{-1}$ values for expulsion of $Nu^-$ from the intermediates **2b** and **2c** derived from the $\alpha$-hydrogen analogues **3-H** and **9-H**. The $k_{-1}$(**2c**)/$k_{-1}$(**2b**) values in 1:1 DMSO–$H_2O$ at 20 °C are 5238 (piperidine), 5000 (morpholine), 11300 ($OH^-$).[12,30a]




However, both predictions were not fulfilled. First, catalysis was not observed in the reactions of ***E*-3-Cl** and ***E*- and *Z*-3-I** with amines. Second, with the poorer nucleofuge and better electron-withdrawing $NO_2$ a slight catalysis ($k_3/k_2$ = 13–100; Table I) was observed for ***E*-3-$NO_2$** in EtOH but not in MeCN, and with morpholine and piperidine but not with aniline. Moreover, amine catalysis was not observed for ***Z*- and *E*-3-$NO_2$** with primary and secondary aliphatic and aromatic amines (including piperidine) in dioxan, MeCN, or MeOH.[12a]

The lack of catalysis for ***E*- and *Z*-3-I** and ***E*-3-Cl** can reflect a lower stability of the nitro compared with the dicyano carbanion in MeCN, as judged by the $pK_a$'s in DMSO.[9b] In terms of eq 9 either $k_2 + k_3[\text{amine}] \gg k_{-1}$ (i.e., $k_{obs} = k_1$) or $k_{-1} > k_2 \gg k_3[\text{amine}]$ (i.e., $k_{obs} = k_1k_2/k_{-1}$) for

(25) For a review of the problem, see: Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1000.
(26) For a review on the rotation around the $C_\alpha$–$C_\beta$ bonds of push–pull ethylenes including enamines, see: Sandstrom, J. *Top. Stereochem.* **1983**, *14*, 83.
(27) Allade, I.; Dubois, P.; Levillain, P.; Viel, C. *Bull. Soc. Chim. Fr.* **1983**, II-339;
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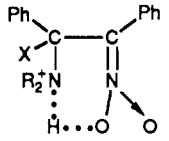
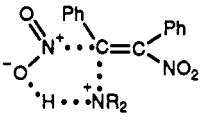
the **3-X** system, but not for **9**. The changes of $k_{-1}$ and $k_2$ in **3** and **9** are parallel (see above) so that the differences are more likely due to the $k_3$ terms. Unfortunately, information is not available in Bernasconi's extensive data[11b,30] on the rate constant analogues to $k_3$ or on the influence of substituents $\beta$ to the $R_2N^+H$ group on the $k_3$ value. Since $k_2$ is relatively high, the lack of catalysis for **3-I** can be due to a low $k_3$[amine] in spite of the relatively high (0.1–1.5 M) amine concentrations used. In addition, the zwitterion derived from **3** is more crowded than that from **9**, which may increase preferentially the $k_{-1}$ term for the former.

Another important difference is that geometry allows intramolecular hydrogen bonding in **10**, Y = $NO_2$, Y′ = Ph (cf. **13a**) but not in **10**, Y = Y′ = CN. The hydrogen



**13a**: $R_2 = -(CH_2)_2G(CH_2)_2-$; G = O, $CH_2$



**13b**

bonding invoked to explain the *Z* stereochemistry of the nitro enamines[27] should be stronger in the zwitterion with the more acidic NH proton. Acidity toward an external amine and presumably $k_3$ will then be reduced. Catalysis for systems **9**, X = Cl, Br, is weak, and compensation or augmentation of these different effects can account for the lack of catalysis for **3-X**, X = Cl, I.

The absence of amine catalysis for ***E*-3-$NO_2$** and ***Z*-3-$NO_2$**, even at high amine concentrations, was ascribed[12a] to the symmetry of these nitroalkenes: the $\beta$-nitro group in **10**, Y = $NO_2$, Y′ = Ph, delocalizes the charge much less than the $\alpha$-nitro group which is the main hydrogen bond acceptor (cf. **13b**). This hydrogen bonding serves as an "intramolecular autocatalysis" by accelerating nucleofuge expulsion, with a consequent elimination of the need for external amine catalysis. However, an identical explanation should also apply for the amine-catalyzed substitutions of 1,2-dinitrobenzene.[29]

Small rate accelerations such as those observed with morpholine and piperidine are not regarded as a strong argument for base catalysis in $S_NAr$ reactions.[31] Moreover, the "catalysis plots" are nonlinear. Hence, the mild rate accelerations may be due to medium effect, in line with Dubois' results.[12a] Nevertheless, it is worthwhile to discuss briefly the rate acceleration as being due to authentic base catalysis. Nitro is a poorer nucleofuge than $Cl^-$ or $I^-$, but it acidifies the ammonium ion moiety in **10** more than the halogens. Consequently, deprotonation of **10** can precede the C–$NO_2$ bond cleavage, and the magnitude of this catalysis will be small, as observed in EtOH. Why, in contrast to the behavior of **9**, X = Cl, F, with amines,[28a,b] was catalysis not observed in MeCN? If intramolecular hydrogen bonding is important in **10**, X = Y = $NO_2$, Y′ = Ph, a six-membered transition state similar to **13a** will become stabilized in MeCN.[32] Competition of intermolecular hydrogen bonding to EtOH with the intramolecular bonding will make expulsion of $NO_2^-$ more difficult from the stabilized zwitterion. Consequently, catalysis is more likely to be observed in EtOH, as found.

**Effect of the Nucleofuge.** The absence of amine catalysis for most reactions of compounds **3** indicates either a rate-determining $k_1$ or a very low $k_3/k_2$ ratio and a composite $k_{obs}$ (eq 10). It is interesting if the change of the nucleofuge can distinguish these alternatives.

$$k_{obs} = k_1k_2/k_{-1} \tag{10}$$

***k*$_{Cl}$/*k*$_{I}$ Ratios.** Significant element effects, i.e., $k_{Cl}/k_I$ = 20.1–23.7, were found with piperidine and morpholine (Table IV). These values differ from the $k_{Br}/k_{Cl}$ ratios, which are mostly close to, or slightly above, unity,[4a,d,33] or from the $k_{OMs}/k_{Cl}$ ratios of 10.4–59.7 found for compounds $p$-$O_2NC_6H_4C(X)=CY_2$ (Y = CN, $CO_2Et$; X = Cl, OMs).[6] The $k_{Cl}/k_I$ ratios with the anionic nucleophiles $p$-$MeC_6H_4S^-$, $NCS^-$, and $N_3^-$ are also >1, being 2.9–5.2, except for a ratio of 0.67 with $N_3^-$ in MeOH at 30 °C.

The polar effect of the two halogens differ only slightly. The $\sigma_I$ values are 0.14–0.16 ($CH_2Cl$) and 0.14–0.18 ($CH_2I$) based on various methods[34] and the $\sigma_R^0$ values are 0.00 ($CH_2Cl$), 0.05 ($CH_2I$) based on IR method.[35a,b] Also $\sigma_I$(Cl) = 0.37–0.48, $\sigma_I$(I) = 0.38–0.47,[34a,35c,d] and $\sigma_R^0$ = –0.18 to –0.22 (Cl) and –0.14 to –0.22 (I).[34c,35a] Consequently, the electrophilicity of $C_\alpha$ of ***E*-3-Cl** is similar or slightly higher than that of ***E*-3-I**. Hence, $k_{Cl}/k_I$ values should be around, or slightly above, unity for a rate-determining $k_1$ and we therefore ascribe a rate-determining bond formation for the anionic nucleophiles. Since the higher ratios with the amines are inconsistent with a rate-determining $k_1$, we will see if they fit eq 10, which for our observed rate ($k_{obs}$) ratios has the form of eq 11.

$$\frac{k_{obs}(\textit{E}\text{-3-Cl})}{k_{obs}(\textit{E}\text{-3-I})} = \frac{k_1(Cl)}{k_1(I)}\cdot\frac{k_2(Cl)}{k_2(I)}\cdot\frac{k_{-1}(I)}{k_{-1}(Cl)} \tag{11}$$

$k_1$(Cl)/$k_1$(I) is approximated by $k_{obs}$(***E*-3-Cl**)/$k_{obs}$(***E*-3-I**) ratios for the anionic nucleophiles, i.e., 0.67–5.2 (Table IV). $k_2$(Cl)/$k_2$(I) is likely to be ≤1, judged by the $k_{Cl}/k_I$ < 1 for saturated compounds[36] coupled with the exothermicity of the C–X bond cleavage in **10**, or by the $k_{Br}/k_{Cl}$ ratios of 2–3 for expulsion of $Cl^-$ and $Br^-$ from carbanions $R_2\bar{C}$-C(Cl)(Br)Nu.[37] Hence, the high $k_{obs}$(***E*-3-Cl**)/$k_{obs}$(***E*-3-I**) ratios reflect a high [$k_{-1}$(I)/$k_{-1}$(Cl)] ratio. This is consistent with a higher steric $R_3N^+/X$ interaction in **10**, X = I, than in **10**, X = Cl, which can lead to $k_{-1}$(I)/$k_{-1}$(Cl) > 1.

The only previous $k_{Cl}/k_I$ ratios in vinylic substitutions are 0.17 and 0.46, respectively, for the reactions of $EtS^-$ with crotononitriles and ethyl crotonate.[38] It is unlikely that they reflect participation of a C–X bond cleavage in the rate-determining step since the variation in the ratios even for a single nucleophile suggests that values < 1 can still be accommodated within the multistep process. Indeed, the analogous $S_NAr$ substitution $k_{Cl}/k_I$ ratios are both higher and lower than unity.[39–43]

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(39) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: Amsterdam, 1968; Chapter 5, pp 137–179.

**$k_{NO_2}/k_{Cl}$ Ratios.** Nitro is not a common nucleofuge in aliphatic substitution, but it is a nucleofuge in $S_{RN}1$[22] and $S_NAr$[39,44] reactions. In vinylic systems quantitative data are available for substitutions of α-chloro-β-nitrostyrenes by amines,[10] 9-nitromethylenefluorene by $MeO^-$ (MeOH) or $CN^-$ (DMF, DMSO),[23b] dinitromethylenefluorene with $N_3^-$,[45] and ***E***- and ***Z*-3-NO₂** with amines.[12a] The data of Table IV are a valuable addition to what is erroneously called "relatively mobility" of the nitro group.

Comparative data are available for $S_NAr$ reactions[39] where nucleophilic attack is rate-determining. The $k_{NO_2}/k_{Cl}$ = 183 and $k_{NO_2}/k_I$ = 510 for the reaction of $MeO^-$/MeOH at 50 °C with $p$-$O_2NC_6H_4X$[42a] and $k_{NO_2}/k_I$ = 78.7 with $N_3^-$/MeOH.[46] For 2,4-$(O_2N)_2C_6H_3X$ with piperidine in MeOH, $k_{NO_2}/k_{Cl}$ = 207, $k_{NO_2}/k_I$ = 882,[47a] and with $PhS^-$ in MeOH $k_{NO_2}/k_I$, $k_{NO_2}/k_{Cl} > 100$.[47b]

The $k_{NO_2}/k_{Cl}$ ratios of 2.8–5.3 with piperidine and morpholine (Table IV) are only qualitatively consistent with a rate-determining $k_1$ since the higher values for $S_NAr$ reactions and comparison of the $\sigma_I(NO_2)$ values of 0.57–0.76[34a,b,48] and $\sigma_R^0(NO_2)$ of 0.17–0.20[47a,48] with those of Cl given above, suggest much higher ratios for a rate-determining $k_1$. However, since $k_{aniline}/k_{Morp}$ ratio is <1, an alternative interpretation is again that $k_{obs}$ is given by eq 10. Analysis in terms of eq 12 approximates the $k_1$-

$$\frac{k_{obs}(\textbf{\textit{E}}\text{-3-NO}_2)}{k_{obs}(\textbf{\textit{E}}\text{-3-Cl})} = \frac{k_1(NO_2)}{k_1(Cl)} \cdot \frac{k_2(NO_2)}{k_2(Cl)} \cdot \frac{k_{-1}(Cl)}{k_{-1}(NO_2)} \quad (12)$$

$(NO_2)/k_1(Cl)$ ratio by the value of 9.7 ± 0.1 obtained $NCS^-$. The third term should be <1 for steric reasons and >1 for electronic reasons. We believe that the second term which involves the C–X bond cleavage is < 1, and it may reduce the first term with amines as nucleophiles.

**$k_{NO_2}/k_I$ Ratios.** The data on ***Z*-3-NO₂**[12a] enables comparison of $k_{NO_2}/k_I$ values for the *E* and the *Z* series. $k$(***Z*-3-NO₂**)(piperidine, MeOH)/$k$(***Z*-3-I**)(piperidine, EtOH) = 6990 at 30 °C. Correction for the solvent change ($k_{EtOH}/k_{MeOH}$ = 1.1 for ***E*-3-NO₂** with piperidine) gives $k_{Z\text{-3-NO}_2}/k_{Z\text{-3-I}}$ = 6380. For the *E* isomer, $k_{E\text{-3-NO}_2}/k_{E\text{-3-X}}$ = 50 with $NCS^-$, 122 with piperidine, and 140 with morpholine in EtOH at 30 °C. The ratios are in the region shown by $S_NAr$ reactions.

In conclusion, the amine catalysis, and the $k_{obs}(NO_2)/k_{obs}(Cl)$ with amine nucleophiles may indicate the participation of the C–$NO_2$ bond cleavage in the rate-determining step with amino nucleophiles. However, the evidence is not compelling and is weakened by the $k_{NO_2}/k_I$ ratios.

***E*-3-I/*Z*-3-I Ratios.** The significant steric interactions between vicinal or geminal substituents in **3** reduce the conjugation of the activating $NO_2$ and Ph groups with the double bond. The differences in ground-state steric and conjugation energies and in the approach of the nucleophile will affect reactivity difference between the *E* and *Z* isomers. A perpendicular approach to ***Z*-3-I** is more hindered, and the lower is the C=C/$NO_2$ conjugation, the lower will be $k_1$. The 2.8-fold higher reactivity of ***E*-3-I** compared with ***Z*-3-I** (Table IV) with $p$-$MeC_6H_4S^-$ is ascribed to these effects and finds precedent in the reactions of ArCH=CHBr with $PhS^-$.[49]

However, with amino nucleophiles the reactivity order in EtOH is inverted and ***Z*-3-I** is 8.3–12.3 times more reactive (Table IV). This is a rare example[42] where the apparently more crowded *Z* isomer is more reactive and may reflect a complex $k_{obs}$ according to eq 10. If expulsions of $I^-$ and amine occur before free rotation in **10**, they will presumably be faster from the zwitterion derived from the *Z* isomer. The much higher *Z*/*E* reactivity ratios of 18–393 for the reaction of ***E***- and ***Z*-3-NO₂** with amines[12a] were ascribed to differences in the ease of formation of intramolecularly hydrogen bonded transition state between the isomers.[50]

**Activation Parameters.** Notwithstanding the temperature inverval used for estimation of the activation parameters, they still add useful information. The $\Delta H^{\ddagger}$ values are not high and the $\Delta S^{\ddagger}$ values are all negative, more so (−39 to −63.5 e.u.) for the amines than for the anionic nucleophiles, except for $N_3^-$. This is expected since the intermediate is zwitterionic with amines and carbanionic with the anionic nucleophiles. Similar trends were observed previously.[4a,6,8,28] The lower $\Delta H^{\ddagger}$ values for the reactions of amines with ***E*-3-NO₂** reflect errors due to the severe extrapolations required to obtain the rate constants. However, together with the highly negative $\Delta S^{\ddagger}$ values, they are also typical for amine-catalyzed reactions,[28] as suggested for ***E*-3-NO₂**.

**Nucleophilicity toward the Nitro Activated Systems.**[3] The nucleophilicities of five anionic (thio and phenoxy) and two neutral (amino) nucleophiles relative to morpholine (our slowest nucleophile) toward ***E*-3-Cl** are given in Table VI. Also given are fewer data for reactions of ***E*-3-I** and ***E*-3-NO₂** and for **3-H** from Bernasconi's work.[11b,30] Our data are limited since $N_3^-$ gives further reaction to **4**, and $MeO^-$[7b] and $R^-$[51] also give a disubstitution product. Our work extends the limited data on nucleophilicities toward vinylic carbon,[3] especially in substitution reactions.

The data reveal the following aspects: (a) The aryl thiolates are $10^3$–$10^4$ more reactive than the oxygen and amino nucleophiles. However, the $SCN^-$ ion is much less reactive than the $ArS^-$ nucleophiles in spite of its increased polarizability. (b) The soft thio nucleophiles are relatively more reactive toward the softer ***E*-3-I** than toward ***E*-3-Cl**. The reactivities of the other nucleophiles with the three substrates seem similar. (c) The $ArO^-$ nucleophiles show moderate reactivity, but the harder $MeO^-$ is apparently much less reactive (see above).[7b] (d) $N_3^-$ is more reactive toward the softer ***E*-3-Cl** than toward (*Z*)-ClCH=C(CN)Ph.[8] (e) The $k_{p\text{-MeC}_6H_4S^-}/k_{p\text{-ClC}_6H_4S^-}$ and the

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$k_{p\text{-}MeC_6H_4O^-}/k_{p\text{-}ClC_6H_4O^-}$ ratios lead to low Hammett's $\rho$ values of −0.88 to −0.91 and −0.95 to −1.11, respectively. These values are reminiscent of those of −0.39 to −1.55 obtained with $ArS^-$ for other vinylic systems.[3,6,8,52] For the $ArS^-$ $\beta_{nuc} = 0.30$ at 30° based on the $pK_a$'s of the ArSH in 95% EtOH[53] whereas $\beta_{nuc} = 0.16$ for addition of aliphatic thiols to ***E*-3-H** in 1:1 DMSO–$H_2O$.[30b] (f) Piperidine and morpholine seem less reactive than toward other vinylic systems. (g) The $k_{Pip}/k_{Morp}$ values of 3.0–5.05 with ***E*-3-X** (X = Cl, I, $NO_2$), and ***Z*-3-I** in EtOH and 6.8–9.5 with ***E*-3-Cl** and ***E*-3-$NO_2$** in MeCN (Table V) are somewhat lower than the values found for amines addition to $CH_2$=CHCN in $H_2O$ (10.1),[54a] to $CH_2$=$CHCO_2Me$ in MeOH (17.4),[54b] or for the substitution of $p$-$O_2NC_6H_4C(X)$=$C(CO_2Et)_2$ (X = OMs, OTs) in MeCN, THF, and EtOH (3.5–22.3).[6] The values for addition to PhCH=$C(CN)_2$ (3.4),[55a] benzylidene Meldrum acid (1.5),[55b] or β-nitrostilbenes (5.8–6.6)[30a] in 50% DMSO–50% $H_2O$ are similar to ours.[3] Using the $pK_a$'s in water (8.33 and 11.12) $\beta_{nuc}$ values in EtOH for our four substrates are very low: 0.17–0.25. Using the $pK_a$'s in MeCN (morpholine 16.61; piperidine 18.92)[56] the $\beta_{nuc}$ values are somewhat higher in MeCN: 0.36–0.39 with ***E*-3-Cl** and 0.36–0.42 with ***E*-3-$NO_2$**. (h) The unusual $k_{Morp}/k_{aniline}$ ratios of 0.65–0.93 with ***E*-3-$NO_2$** in EtOH are in apparent contrast to a rate-determining $k_1$ even when the steric difference between the amines is considered since morpholine is much more basic than aniline. The protic solvent is apparently responsible, since related ratios are normal in aprotic solvents: $k_{Morp}/k_{p\text{-toluidine}} = 21.6$ in the reactions with (*E*)-PhC(Cl)=$CHNO_2$ in MeCN, whereas $k_{Pip}/k_{p\text{-toluidine}} = 89$ with ***E*-** and ***Z*-3-$NO_2$** in MeCN, but only 1.3–1.38 in MeOH.[12a] This difference for **3-$NO_2$** may be connected with the formation of **13b**.[12a] An alternative is an intervention of the $k_{-1}$ step which may be more important with morpholine than with aniline.

A revealing comparison is that of the nucleophilicity "scales" for the substitution of ***E*-3-Cl** in EtOH, and of compounds **14** in MeOH at 0 °C[52a] or **15** in EtOH at 30 °C,[8] as given in Table X of ref 3. Unfortunately, only $p$-$TolS^-$, other $ArS^-$ ions, piperidine, and $N_3^-$ are common to the three scales. Neverthless, it is clear that the more

(*Z*)-$TolSO_2CH$=CHCl (**14**) (*Z*)-ClCH=C(CN)Ph (**15**)

electrophilic the alkene, the higher the reactivity spread. The $k_{p\text{-}TolS^-}/k_{Pip}$ ratios are 1.1 for **14**, 191 for **15**, 13625 for ***E*-3-Cl**, and 86970 for ***E*-3-I**; the $k_{N_3^-}/k_{Pip}$ values are 0.024 for **14**, 0.041 for **15**, 11.8 for ***E*-3-Cl**, and 473 for ***E*-3-I** ($N_3^-$ in MeOH for the last two values), and the $k_{Pip}/k_{RO^-}$ values are 9.1 for **14**, ca. 1 for **15**, and >10 for ***E*-3-Cl**.[7b] Consequently, the softer (more electrophilic) the vinylic substrate the higher its reactivity with the softer ($ArS^-$) nucleophile and the lower its reactivity with the hard ($RO^-$) nucleophile.

The role of a soft nucleofuge in extending the reactivity range is shown by comparing the $k_{TolS^-}/k_{Pip}$ value of 86970 for ***E*-3-I** in EtOH with the $k_{EtS^-}/k_{Pip}$ with ***E*-3-H** in 1:1 DMSO–$H_2O$.[30] The $k_{p\text{-}TolS^-}/k_{Pip}$ with ***E*-3-H** ratio would be even lower, as judged by the $pK_a$'s (EtSH 10.5; $p$-TolSH 6.52 in water).[57] Both steric effects which are more pronounced in ***E*-3-I** and "symbiotic" soft–soft interactions which involve the nucleofugic moiety seem important. Comparison with the α-methoxy analogue ***E*-3-OMe**[13b] gives $k_{E\text{-}3\text{-}H}/k_{E\text{-}3\text{-}OMe} = 149$ with $HOCH_2CH_2S^-$ in 1:1 DMSO–$H_2O$. It is difficult without additional data to dissect this difference to the contribution of the hard MeO group and to resonative positive charge dispersal by the oxygen, analogous to that shown in **8b**.

**Table VIII. $\beta_{nuc}$ Values for Addition of Thiolate Anions and Amines to Electrophilic Alkenes**

| alkene | solvent | $\beta_{nuc}$ for $RS^-$ | $\beta_{nuc}$ for $RNH_2$[a] | ref |
|---|---|---|---|---|
| (*E*)-PhCH=$C(NO_2)$Ph | 1:1 DMSO–$H_2O$ | 0.16 | 0.34 | 27 |
| $CH_2$=CHCN | $H_2O$ | 0.45 | 0.43[c] | *d* |
| PhCOCH=CHOMe | | | 0.4 | *e* |
| (*E*)-PhC(CN)=CHCl | EtOH | 0.17[b] | 0.3 | 8 |
| (*Z*)-PhC(CN)=CHCl | EtOH | 0.20[b] | 0.29 | 8 |
| (*E*)-PhC(Cl)=$C(NO_2)$Ph | EtOH | 0.30[b] | 0.17 | |
| | MeCN | | 0.36 | pw[f] |
| (*E*)-PhC(I)=$C(NO_2)$Ph | EtOH | | 0.18 | pw[f] |
| (*Z*)-PhC(I)=$C(NO_2)$Ph | EtOH | | 0.24 | pw[f] |
| (*E*)-PhC($NO_2$)=$C(NO_2)$Ph | EtOH | | 0.18 | pw[f] |
| | MeCN | | 0.36 | pw[f] |

[a] Based on the pair piperidine/morpholine unless otherwise stated. [b] Based on the pair $p$-$YC_6H_4S^-$, Y = Cl, Me. [c] For several aliphatic amines. [d] Friedman, M.; Cavins, J. F.; Wall, J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3672. [e] Ritchie, C. D.; Kawasaki, A. *J. Org. Chem.* **1981**, *46*, 4704. [f] Present work.

In Table VIII we collected all the $\beta_{nuc}$ values known to us in nucleophilic vinylic reactions. The presence of the nucleofuge distinguishes the substitution from the addition reaction by contributing an added softness (X = I, Cl, Br) or hardness (OMs, OTs), presumably modifying the soft/hard nucleophile reactivity ratio. This can explain why $\beta_{nuc}(RS^-) > \beta_{nuc}$(amines) with ***E*-3-Cl** and vice versa with ***E*-3-H**. The low $\beta_{nuc}$ values for both types of nucleophiles may suggest an early transition state for the Nu–C bond-forming step, but in the absence of data on isotope effects in this step, the reversal in the relative value for ***E*-3-H** and ***E*-3-Cl** and in view of the criticism of using $\beta_{nuc}$ as a measure of transition-state structure[58] we will follow Bernasconi and Killion[30b] in refraining from using our data as a probe for the transition-state structure.

**Reaction with Azide Ion.** Second-order kinetics is obtained in the reaction of ***E*-3-Cl** and ***E*-3-I** with $N_3^-$ (Table II), whereas the reaction is zero order in $[N_3^-]$ with ***E*-3-$NO_2$** at 30 °C, and a 6-fold increase in $[N_3^-]$ increases $k_1$ 1.7-fold at 45 °C (Table III). Consequently, the process measured with the vinyl halides differs from that with the nitroalkene. With ***E*-3-Cl** and ***E*-3-I**, the step measured is the nucleophilic attack leading to the vinyl azide, which then cyclizes to **4**. With ***E*-3-$NO_2$** the first-order process probably measures the cyclization–dediazonization of the α-nitro-β-azidostilbene to the furoxan **4**.[59]

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Table IX. Analytical Data for PhC(X)=C(Ph)$NO_2$

| X | yield, % | mp, °C | color | cryst solvent | analysis: found C | H | N | hal | S | formula | required: C | H | N | hal | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $OC_4H_8N$[a] | 93 | 213–4 | yellow plates | EtOH | 69.48 | 5.77 | 9.20 | | | $C_{18}H_{18}N_2O_3$ | 69.68 | 5.81 | 9.04 | | |
| $C_5H_{10}N$[b] | 91 | 172–3 | orange needles | EtOH | 73.83 | 6.64 | 8.84 | | | $C_{19}H_{20}N_2O_2$ | 74.07 | 6.48 | 9.08 | | |
| SCN | 89 | 196 | yellow needles | EtOH | 63.86 | 3.76 | 9.74 | | 11.28 | $C_{15}H_{10}N_2O_2S$ | 63.90 | 3.54 | 9.92 | | 11.32 |
| p-$ClC_6H_4S$ | 87 | 108–9 | yellow needles | pe[c] | 65.62 | 3.76 | 4.11 | 9.09 | 8.57 | $C_{20}H_{14}NClO_2S$ | 65.35 | 3.80 | 3.80 | 9.65 | 8.70 |
| p-$MeC_6H_4S$ | 93 | 125–7 | yellow needles | pe[c] | 72.70 | 4.90 | 3.84 | | 9.25 | $C_{21}H_{17}NO_2S$ | 72.61 | 4.93 | 4.03 | | 9.21 |
| p-$ClC_6H_4O$ | 72 | 125–7 | yellow needles | MeOH | 68.56 | 4.21 | 4.05 | 10.08 | | $C_{20}H_{14}NClO_3$ | 68.30 | 3.98 | 3.98 | 10.10 | |
| p-$MeC_6H_4O$ | 75 | 122–3 | white needles | MeOH | 75.90 | 5.48 | 3.91 | | | $C_{21}H_{17}NO_3$ | 76.12 | 5.17 | 4.23 | | |

[a] Morpholino. [b] Piperidino. [c] Petroleum ether.

**Solvent Effects.** The $k_{EtOH}/k_{MeOH}$ values for substitution of ***E*-3-Cl** are 2.18 ± 0.06 with p-$MeC_6H_4S^-$ and 1.01 ± 0.02 with piperidine. A ratio > 1 for the $ArS^-$ reaction and < 1 with piperidine are expected in the lower dielectric EtOH. The lack of solvent effect with piperidine suggests that formation of stronger hydrogen bonds between the amine and MeOH compensates for a rate increase due to the higher dielectric constant. The low $k_{MeCN}/k_{EtOH}$ ratio of 1.50 ± 0.20 in the reaction of ***E*-3-Cl** with $CNS^-$ is ascribed to a lower reactivity due to solvation of $CNS^-$. Amines show moderate rate decrease: $k_{MeCN}/k_{EtOH}$ = 16.7 ± 8.2 (***E*-3-Cl** + piperidine), 6.2 ± 2.4 (***E*-3-Cl** + morpholine), 23.8 ± 4.1 (or 18.3[12a]) (***E*-3-$NO_2$** + piperidine), 12.3 ± 2.4 (***E*-3-$NO_2$** + morpholine). Similar results were reported for ***Z*-** and ***E*-3-$NO_2$** with aliphatic amines, but opposite results with p-toluidine.[21a] This was ascribed to formation of MeOH–$HNR_2$ hydrogen bonds which reduce the amine nucleophilicity[12a] and similar interaction in EtOH coupled with strong intramolecular hydrogen bond formation in the transition state leading to **10** apparently applies in our case. The low $k_{dioxan\text{-}H_2O}/k_{MeOH}$ ratios of 2.1 ± 0.1 for ***E*-3-Cl** and 0.91 ± 0.02 for ***E*-3-I** in the reaction with $N_3^-$ fit a rate-determining formation of the vinyl azide.

**Effect of the α-Electron-Withdrawing Substituent.** The substitution rates of ***E*-3-Cl** and **15** enables an hitherto unavailable comparison of the activating effects of $NO_2$ and CN in vinylic substitution. By using the $\sigma\rho$ relationship, $k(ClCH{=}C(CN)_2)/k(PhC(Cl) = C(CN)_2) = 4.18 \times 10^5$ in the reaction with p-$NCC_6H_4NH_2$ in MeCN.[6] If steric and solvent effects are neglected, the relative $k$(***E*-3-Cl**)/k(**15**) is ca. $10^5$ with p-$MeC_6H_4S^-$, showing, in analogy to nucleophilic addition to electrophilic olefins,[60] that $NO_2$ is much more activating. This relative reactivity is much lower than expected from the $pK_a(MeCN) - pK_a(MeNO_2)$ of 14 in water[9a] or DMSO.[9b] This "lower" reactivity of our nitro-activated system finds precedents in nucleophilic vinylic additions[11b,61] and in an E1cB elimination.[62] The lower reactivity can be ascribed to an imbalance in the development of Nu–$C_\beta$ bonding and formation of charge on the nitro group in the transition state.[11b,63] Alternatively, reduced planarity of ***E*-3-Cl** by steric effects results in reduction of the electrophilicity of $C_\alpha$. Indeed, when an α-H is replaced by an α-Ph, the rate with morpholine is reduced appreciably: $k(PhC(Cl){=}CHNO_2)/k(PhC(Cl){=}C(Ph)NO_2) = 171$.[6] Consequently, the lower ground-state energy due to the additional π-(C=C)-π(Ph) conjugation and the higher steric hindrance to the nucleophilic attack on ***E*-3-Cl** overcome the combination of relief of cis interactions accompanying the $sp^2 \rightarrow sp^3$ change in the substitution, and the added stabilizing negative charge dispersal by the α-Ph in ***E*-3-Cl**.

## Experimental Section

**Spectral Measurements.** UV spectra were measured with a Perkin-Elmer 332 spectrophotometer, IR spectra with a Perkin-Elmer 337 spectrophotometer, mass spectra with a MAT 311 instrument, and NMR spectra with Varian T-60 or HA-100 instruments.

**Solvents.** Acetonitrile (Baker Analyzed) was dried for 1 day over $P_2O_5$, refluxed for 5 h over $P_2O_5$, and distilled through a fractionating column, and the middle fraction, bp 78 °C, was used. Ethanol (Frutarom), bp 78 °C, and methanol (Frutarom), bp 65 °C, were dried according to Vogel.[64]

**Kinetic Procedure.** Stock solution of the reactants were prepared daily. The samples were mixed at the reaction temperature, and the reactions were followed in the thermostatically controlled chamber of a Gilford 2400-S spectrophotometer. Measurements were conducted either at the $\lambda_{max}$ of the product or at a longer wavelength in order to avoid corrections for the absorption of the free nucleophile.

The pseudo-first-order coefficients in the presence of excess of nucleophile were calculated with the aid of the KINDAT programme.[65] The correlation coefficients $r$ were >0.9999. $k_{obs}$ values were obtained by dividing the first-order coefficients by the nucleophile concentration.

**(*E*)-β-Chloro-α-nitrostilbene (*E*-3-Cl)**, mp 144 °C, was prepared according to Iwai, Tomita, and Ide.[14] (lit.[14] mp 144–144.5 °C). The compound was pure according to GLC over 20% SE-30 column (2 m) on Chromosorb W 60-80. Anal. Found: C, 64.72; H, 3.88; N, 5.26; Cl, 13.63. Calcd for $C_{14}H_{10}NClO_2$: C, 64.77; H, 3.86; N, 5.39; Cl, 13.67. UV (MeCN) $\lambda_{max}$: 245 nm (ε 11 900). IR (KBr) $\lambda_{max}$: 1445 (s, $NO_2$) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 7.33–7.40 (d). Mass spectra, $m/z$ (relative abundance, assignment): 261, 259 (6, 17, M), 215, 213, (17, 49, M – $NO_2$), 178 (100, M – $NO_2$ – Cl), 176 (24), 151 (12), 105 (15).

**(*Z*)- and (*E*)-β-iodo-α-nitrostilbenes (*Z*- and *E*-3-I)** were prepared according to Stevens and Emmons.[15] ***Z*-3-I**, mp 118 °C (lit.[15] mp 113–114 °C) was purified by thin-layer chromatography on silica using 10% acetone–90% petroleum ether as eluent. UV (EtOH) $\lambda_{max}$: 240 (ε 15 200), 310 nm (ε 4400). IR (KBr) $\lambda_{max}$: 1525, 1450, 1370, *815*, *790*, 765, 730, 695 (all s) $cm^{-1}$. (The italicized bands distinguish the compound from ***E*-3-I**). $^1H$ NMR ($CDCl_3$): δ 7.22 (s, Ph). Mass spectrum $m/z$ (relative abundance,

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**Table X. Spectral Properties of the Substitution Products, PhCX=C($NO_2$)Ph**

| X | $\lambda_{max}^{MeCN}$, nm ($\epsilon$)[a] | δ ($CDCl_3$) Ph[b] | Ph[b] | X | m/e (assignment, relative abundance) |
|---|---|---|---|---|---|
| $OC_4H_8N$ | 298 (7400), 405 (9700) | 7.25 | 7.15 | 3.72 (4 H, m), 3.00 (4 H, m) | 310 (M, 7), 264 (M - $NO_2$, 9), 189 (23), 178 ($Ph_2C_2^+$, 13), 105 ($PhCO^+$, 100), 103 (PhCN, 93), 77 (Ph, 67) |
| $C_5H_{10}N$ | 290 (6900), 408 (9800) | 7.17 | 6.97 | 2.97 (4 H, m), 1.67 (6 H, m) | 308 (M, 31), 275 (21), 262 (M - $NO_2$, 22), 188 (60), 178 ($Ph_2C_2^+$, 15), 105 ($PhCO^+$, 100), 104 (PhCN, 94), 77 ($Ph^+$, 77) |
| SCN | 249 (8600), 312 (2500)[c] | 7.07 | 7.02 | | 282 (M, 12), 235 (M - $NO_2$, 32), 224 (M - SCN, 10), 178 ($Ph_2C_2^+$, 100), 176 ($Ph_2C_2^+$ - $H_2$, 20), 105 ($PhCO^+$, 35), 77 (Ph, 22) |
| p-$ClC_6H_4S$ | 254 sh (13100), 327 (9800) | 6.77–7.17 (m) | | | For $^{35}Cl$: 367 (M, 7), 336 (14), 286 (M - Cl - $NO_2$, 34), 178 ($Ph_2C_2^+$, 80), 77 ($Ph^+$, 38) |
| p-$MeC_6H_4S$ | 255 sh (10200), 337 (7700) | 6.90 | 6.69 | 8.05 (4 H, Ar), 2.10 (s, Me) | 347 (M, 3), 317 (M - NO, 9), 286 (M - $NO_2$ - Me, 23), 178 ($Ph_2C_2^+$, 58), 152 (15), 139 (88), 123 ($SC_6H_4Me$, 18), 105 ($PhCO^+$, 100), 103 (PhCN, 30), 77 ($Ph^+$, 42) |
| p-$ClC_6H_4O$ | 232 (20500), 270 (12400) | 7.05–7.30 (m) | | | 189 (15), 178 ($Ph_2C_2^+$, 24), 123 (26), 111 (38), 109 (40), 105 ($PhCO^+$, 10), 103 (PhCN, 100) |
| p-$MeC_6H_4O$ | 220 (25400), 264 (11300) | 6.75–7.09 (m) | | 2.14 (s, Me) | 331 (M, 0.2), 178 ($Ph_2C_2^+$, 23), 107 (30), 105 ($PhCO^+$, 100), 103 (PhCN, 37), 77 ($Ph^+$, 70) |

[a] All the compounds have the following absorptions in the IR: $\nu_{max}$ (KBr) 3060–3020 (C—H, w), 1600–1630 (C=C, w), 1530–1565, 1295, 1305 (s, $NO_2$) $cm^{-1}$. [b] Singlet unless otherwise stated. [c] $\nu_{max}$ (Nujol): 2160 (s) $cm^{-1}$.

assignment): 351 (1, M), 294 (20), 195 (96), 180 (96), 179 (97), 178 (84, M - I - $NO_2$), 177 (99), 167 (50), 166 (50), 153 (98), 152 (98), 151 (68), 127 (82), 105 (100).

***E*-3-I**, mp 189 °C (lit.[15] mp 175–176 °C), was purified by thin-layer chromatography. Anal. Found: C, 47.90; H, 2.89; N, 3.86; I, 36.60. Calcd for $C_{14}H_{10}INO_2$: C, 47.86; H, 2.84; N, 3.99; I, 36.18. UV (EtOH) $\lambda_{max}$: 242 sh ($\epsilon$ 13700), 310 nm ($\epsilon$ 2300) (identical with the literature values). IR (KBr) $\lambda_{max}$: 1520 (s), 1445 (m), 1350 (m), 760 (m), 745 (m), 695 (s) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 7.47–7.73 (m). Mass spectra m/z (relative abundance, assignment): 351 (2, M), 294 (11), 196 (18), 195 (44), 180 (45), 179 (100), 178 (36, M - I - $NO_2$), 177 (44), 127 (36), 106 (79).

***E*-3-$NO_2$** was prepared as pale yellow plates, mp 187–188 °C, according to Campbell et al.[16] UV (EtOH) $\lambda_{max}$: 240 nm sh ($\epsilon$ 12900) [lit. 238 nm sh ($\epsilon$ 13300)]. IR (KBr) $\lambda_{max}$: 1610–1595 (vw), 1530, 1445, 1350, 760, 755, 700, 690 (all s) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 7.52 (s). Mass spectra m/z (relative abundance, assignment): 270 (3, M), 225 (5, M - $NO_2$), 179 (99), 178 (99, M - $(NO_2)_2$), 177 (73, M - $HNO_2$ - $NO_2$), 176 (99, M - $2HNO_2$), 165 (45), 152 (96), 151 (70), 150 (42), 139 (43), 128 (15), 127 (15), 126 (51), 106 (80), 105 (100, $PhCO^+$).

**Preparation of the Substitution Products. (a) Enamines.** The amine (2–10 equiv) was added to 1 equiv of the vinylic substrate (200 mg) in dry acetonitrile until the formation of a homogeneous solution. The ammonium salt which was formed slowly was filtered off after 1–12 h. The residue was either crystallized directly or after evaporation of the solvent the remainder was dissolved in dry ether, filtered, and evaporated, and the oil obtained was recrystallized or purified by chromatography. The anilino enamine is a known compound.[66]

**(b) Vinyl Thiolates.** The thiol (1.1 equiv) and NaOEt (1.1 equiv) and 1 equivalent of the vinyl halide (200 mg) were reacted in ethanol. After 1 h the solutions were filtered and the solvent was evaporated. The remainder was dissolved in ether, washed with 5% HCl and water, and dried ($MgSO_4$), the ether was evaporated, and the remainder was crystallized or chromatographed.

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**(c) Vinyl Phenolates.** The vinyl phenolates were prepared from the reaction of a 1:1:1 mixture of phenol, NaOEt, and vinyl halide (200 mg) in EtOH. Workup was similar to that described for the vinyl thiolates. The compounds were then crystallized.

**(*E*)-β-Thiocyanato-α-nitrostilbene (*E*-3-CNS).** A 10:1 mixture of KCNS and ***E*-3-Cl** was kept in MeCN for 12 h at 25 °C, or a 10:1 mixture of KCNS and ***E*-3-I** was kept for 5 days at 25 °C. The precipitated KCl or KI were filtered, and the solvent was evaporated. The remainder was dissolved in ether (7 × 50 $cm^3$), washed with water, and dried ($MgSO_4$), the ether was evaporated, and the crude solid was recrystallized from EtOH.

The analytical and spectral data for the substitution products are given in Tables IX and X.

**3,4-Diphenylfuroxan.** A solution of $NaN_3$ (250 mg, 3.85 mmol) in 2:1 acetone–water (50 mL) was added slowly at 0 °C to a solution of ***E*-3-Cl** (100 mg, 0.38 mmol) in 2:1 aqueous acetone (50 mL). The solution immediately became yellow, and gas was evolved. After standing overnight the acetone was evaporated, and the remainder was extracted with ether (3 × 50 $cm^3$), washed with water, and dried ($MgSO_4$). The solvent was removed in vacuo, and the remaining solid was recrystallized from ethanol, giving 71 mg (78%) of **4**, mp 118 °C (lit.[18] mp 117 °C). UV (MeCN) $\lambda_{max}$: 235 ($\epsilon$ 18100), 276 nm ($\epsilon$ 5700). IR (KBr) $\lambda_{max}$: 3060 (w), 1590 (s), 1570 (s) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 7.50 (s, Ar). Mass spectra m/z (relative abundance, assignment): 238 (21, M), 178 (100, M - $N_2O_2$), 176 (22, M - $N_2O_2$ - 2H).

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**Registry No.** (*E*)-**3**-Cl, 57337-95-8; (*E*)-**3**-I, 55902-54-0; (*Z*)-**3**-I, 73013-87-3; (*E*)-3-$NO_2$, 16906-54-0; (*E*)-**3**-SCN, 123126-14-7; (*E*)-3-$SC_6H_4Me$-*p*, 73013-89-5; (*E*)-**3**-Pip, 73013-90-8; (*E*)-**3**-Morp, 73013-91-9; (*Z*)-**3**-OMe, 96746-57-5; (*E*)-**3**-OMe, 96746-56-4; (*E*)-3-$SC_6H_4Cl$-*p*, 85296-26-0; (*E*)-3-$OC_6H_4Cl$-*p*, 123126-15-8; (*E*)-3-$OC_6H_4Me$-*p*, 123126-16-9; **4**, 5585-14-8; Pip, 110-89-4; Morp, 110-91-8; *p*-$ClC_6H_4ONa$, 1193-00-6; *p*-$MeC_6H_4ONa$, 1121-70-6; *p*-$ClC_6H_4SNa$, 18803-44-6; *p*-$MeC_6H_4SNa$, 10486-08-5; KSCN, 333-20-0; $PhNH_2$, 62-53-3; $NaN_3$, 26628-22-8; NaOMe, 124-41-4.