previously. GLC analysis (column 2) indicated that the cis and trans isomers of 5-ethylidene-2-norbornene were the sole reaction products. The identity of the latter was confirmed by GLC spiking with authentic material (Aldrich) and GC/MS. The concentrations of base and olefin were 0.6 and 0.4 M in $Me_2SO$, respectively. The starting material (Aldrich) is actually a mixture of 69.4% endo and 30.6% exo isomers which isomerize at different rates. The results are given in the text.

**Alkylation of Ethyl Acetoacetate.** To a dry 500-mL three-necked flask under nitrogen fitted with a condenser, an addition funnel, and a magnetic stirrer was added KH (22%, 14.5 g, 0.08 mol). The suspension was washed twice with pentane (50 mL) and once with THF. After removal of most of the solvent, fresh THF (100 mL) was added. Pinanol (12.6 g, 0.082 mol) was added carefully over a 10-min period. When the reaction ceased, ethyl acetoacetate (10.6 g, 0.082 mol) and *n*-decane (10 g) in THF (100 mL) were added dropwise with stirring. When the addition was complete, the reaction mixture was brought to reflux, and *n*-butyl iodide (15.0 g, 0.082 mol) was added. Aliquots were removed at intervals and titrated. GLC analysis (column 2) of the reaction mixture was used to calculate the product yield from the internal standard which was corrected for the difference in response factors. A similar procedure was carried out for *t*-BuOK (Ventron) which was freshly sublimed.

**2-Pinanyl Ethers.** The reactions of the alkoxides with *n*-octyl bromide were carried out in $Me_2SO$ at 70 °C.[45] In each case a single long retention time product, the alkyl ether, was observed along with a mixture of octenes at shorter retention time (column 2). The ratio of octenes varied with reaction time and base. The octyl ethers were identified by GC/MS. *cis*-2-Pinanyl octyl ether: $m/e$ (relative intensity) 71 (100), 43 (86), 41 (72), 93 (51), 81 (50), 99 (43), 57 (38), 266 (1, $M^+$). *trans*-2-Pinanyl octyl ether: $m/e$ (relative intensity) 71 (100), 43 (85), 93 (82), 41 (71), 99 (41), 81 (40), 69 (39), 57 (38), 266 (2, $M^+$).

Benzyl chloride (27.3 mmol) was added to a solution of the alkoxide (27.3 mmol) in THF (25 mL) containing dodecane (2.0 g). The reaction was stirred at 30 °C for 5 h and analyzed by GLC (column 2). *t*-BuOK gave 94.4% of the theoretical yield of *tert*-butyl benzyl ether[46] at 58.8% conversion. *cis*-PinOK gave 72.2% of the theroetical yield at 56.2% conversion of *cis*-2-pinanyl benzyl ether: bp 170 °C (10 mm); NMR ($CDCl_3$) $\delta$ 0.94 (s, 3 H), 1.22 (s, 3 H), 1.28 (s, 3 H), 1.4–2.4 (m, 8 H), 4.24 (AB q, 2 H, $J$ = 11 Hz $\nu_A - \nu_B = 0.11$), 7.25 (s, 2 H); mass spectrum, $m/e$ (relative intensity) 93 (100), 91 (98), 79 (69), 77 (52), 41 (42), 108 (40), 107 (39), 92 (31). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.79; H, 10.03. *trans*-PinOK gave 89.3% of the theoretical yield at 61.5% conversion of *trans*-2-pinanyl ether: bp 170 °C (10 mm); NMR ($CDCl_3$) $\delta$ 1.1 (s, 3 H), 1.2 (s, 3 H), 1.26 (s, 3 H), 1.5–2.5 (m, 8 H), 4.32 (s, 2 H), 7.28 (s, 5 H); mass spectrum, $m/e$ (relative intensity) 91 (100), 93 (33), 43 (30), 95 (19), 136 (19), 92 (18), 41 (17), 79 (15). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.60; H, 9.88.

**Isolation of the Alkoxides 1b and 2b.** The physical properties of the pinanoxides have not yet been studied in detail. *cis*-PinOK yielded a pale yellow amorphous solid on isolation, while *trans*-PinOK was a pale brown waxy solid. A 1:1 solid THF complex was obtained from *trans*-PinOK but was not formed with *cis*-PinOK.

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**Registry No. 1a**, 4948-28-1; **1b** (M = K), 72611-32-6; **2a**, 4948-29-2; **2b** (M = K), 72611-33-7; **7a**, 464-41-5; **7b**, 54353-49-0; **9**, 72611-34-8; **12**, 99-87-6; **13**, 32162-27-9; **14**, 1674-08-4; **15**, 38211-97-1; **18**, 138-86-3; **19**, 586-62-9; **20**, 99-86-5; **21**, 99-85-4; **22**, 586-63-0; **23**, 586-67-4; *endo*-5-vinyl-2-norbornene, 25093-48-5; *exo*-5-vinyl-2-norbornene, 23890-32-6; *cis*-5-ethylidene-2-norbornene, 28304-66-7; *trans*-5-ethylidene-2-norbornene, 28304-67-8; *cis*-2-pinanyl octyl ether, 72611-35-9; *trans*-2-pinanyl octyl ether, 72611-36-0; *cis*-2-pinanyl benzyl ether, 72611-37-1; *trans*-2-pinanyl benzyl ether, 72611-38-2.

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# Brønsted Plots in the Reactions of 2,4-Dinitrophenyl Acetate and Methyl Phenyl Carbonate with Substituted Pyridines

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Rate constants are reported for nucleophilic attack of a series of 3- or 4-substituted pyridines on 2,4-dinitrophenyl acetate and methyl phenyl carbonate at 25 °C, and ionic strength 0.2 M. The Brønsted plot obtained is curved for the acetate and linear for the carbonate. The first shows two linear regions (at low and high $pK_a$ values with slopes 0.85 and 0.2, respectively) and a curvature in between. The Brønsted slope for the carbonate is 1.3. The Brønsted curve can be accounted for in terms of a tetrahedral intermediate in the reaction path and a change in the rate-determining step from breakdown of the intermediate to its formation, as the substituted pyridine becomes more basic. A semiempirical equation based on these assumptions fits the experimental data. From the shape of the curved Brønsted plot, an equal leaving ability from the tetrahedral intermediate for 2,4-dinitrophenolate and a (hypothetical) pyridine of $pK_a = 7.3$ is deduced. The influence of the group that does not leave on the relative leaving abilities of phenolates and pyridines is discussed.

Curved Brønsted plots obtained in nucleophilic reactions of carbonyl compounds have often been interpreted in terms of a tetrahedral intermediate in the reaction path and a change in the rate-determining step from leaving-group expulsion to attack by the nucleophile as the nucleophile becomes more basic.[1-6] Quantitative evaluation of the relative leaving abilities of pyridines and chloride anion,[5] thiol and oxygen anions,[3] quinuclidines and phenolates,[4] and pyridines and phenolates[6] from a tetrahedral intermediate has been attempted from semiempirical equations based on the above assumptions.

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In order to study the influence of the group that does not leave on the relative leaving abilities of pyridines and 2,4-dinitrophenolate and phenolate from a tetrahedral intermediate, we chose the reactions of 2,4-dinitrophenyl acetate with substituted pyridines for comparison with the ones of 2,4-dinitrophenyl methyl carbonate[6] and 2,4-dinitrophenyl phenyl carbonate,[4] and the reactions of substituted pyridines with methyl phenyl carbonate for comparison with the ones with phenyl acetate.[1]

Although the rate constants for the reactions of 2,4-dinitrophenyl acetate with three substituted pyridines reported here have been previously measured under slightly different conditions,[1] we wished to obtain a series of rate constants determined under a single set of experimental conditions and to greatly expand the p$K_a$ range covered by the series.

## Experimental Section

**Materials.** The substituted pyridines and other reagents used were purified as described previously.[5] Water was distilled and boiled to remove dissolved carbon dioxide.

2,4-Dinitrophenyl acetate was prepared by a modification of a reported procedure for the acetylation of amines.[7] 2,4-Dinitrophenol (5 g) was dissolved in acetic anhydride (20 mL). A few drops of concentrated sulfuric acid were added, and the mixture was refluxed for 1 h. The mixture was then cooled, poured slowly over cold water (60 mL), and then boiled to decompose the excess acetic anhydride. After cooling, the mixture was filtered and the insoluble residue washed with cold water and finally recrystallized in water. The final product was identified by NMR spectroscopy (mp 70 °C, lit.[8] mp 72 °C).

Methyl phenyl carbonate was prepared by dissolving phenol (10 g) in 1 N sodium hydroxide (100 mL). After the solution was cooled in an ice bath, methyl chloroformate (10 mL) was added dropwise with stirring. The temperature was kept under 10 °C during the addition. After the solution was stirred for 2 h at room temperature, it was dried over anhydrous calcium sulfate and then distilled. The final product was identified by NMR spectroscopy.

**Kinetic Methods.** The reactions of 2,4-dinitrophenyl acetate (DNPA) were followed by measuring the 2,4-dinitrophenolate appearance at 400 nm by means of a Pye Unicam SP 1800 spectrophotometer. The reactions were initiated by injecting 10–20 $\mu$L of a stock solution of DNPA in acetonitrile into 3 mL of the nucleophile aqueous solution in 1-cm cuvettes thermostatted at 25.0 ± 0.1 °C. The injections were performed by means of a Unimetrics 50-$\mu$L syringe provided with a Kloehn adaptor for reproducibility within 0.2%. The initial concentration of the ester was $5 \times 10^{-6}$ M in all runs.

The reactions of methyl phenyl carbonate (MPC) were studied colorimetrically following phenol release (4-aminoantipyrine test).[9] To 15 mL of the aqueous nucleophilic solution in a stoppered flask thermostatted at 25.0 ± 0.1 °C, 75 $\mu$L of a stock solution of MPC in acetonitrile was injected by means of a Unimetrics 100-$\mu$L syringe provided with a Kloehn adaptor. A 0.5-mL aliquot of the reaction mixture, which contained $6.3 \times 10^{-4}$ M methyl phenyl carbonate initially, was added to a freshly prepared aqueous solution consisting of 4.3 mL of 0.014% 4-aminoantipyrine and 0.1 mL of 2 N ammonia. After this mixture was stirred, 0.1 mL of 2% potassium ferricyanide was added and the absorbance read at 505 nm. A calibration curve confirmed the validity of Beer's law in the region of $(0.1\text{–}8.0) \times 10^{-4}$ M phenol.

The final acetonitrile concentration in the reaction mixtures was less than 0.5%. All runs were carried out at an ionic strength of 0.2 M, maintained with sodium perchlorate (DNPA) or potassium chloride (MPC). Most of the reactions were carried out in phosphate buffer solutions at about pH 7. No external buffers were used in the reactions of DNPA with pyridine and 3- and 4-methylpyridines.

Some of the reactions were repeated by the addition of a second aliquot of DNPA or MPC to a reaction mixture in which the corresponding phenolate had already been produced in the first reaction. The rate constants observed for both reactions agreed within experimental error. This check was necessary in order to avoid wrong determinations of rate constants due to a possible inhibition caused by the back-reaction of 2,4-dinitrophenolate or phenolate with the *N*-acetyl- or *N*-methoxycarbonylpyridinium ion intermediate.[1]

All runs were carried out in the presence of a large excess of the substituted pyridine. Pseudo-first-order rate constants ($k_{\text{obsd}}$) were obtained by means of Guggenheim or "infinity" plots; most of these were linear to at least 3 half-lives. Infinity readings were taken after 7–10 half-lives. The experimental conditions for the rate determinations and the $k_{\text{obsd}}$ are summarized in Tables I and II.

**Product Studies.** One of the final products of the reactions of DNPA with 4-(dimethylamino)- and 3-chloropyridines at pH 7.5 was identified as 2,4-dinitrophenolate by comparison of the UV spectra of the reaction samples at "infinity" time with the ones of authentic sample [region scanned: 280–480 nm, $\lambda_{\max}$ 360 nm ($\epsilon_{\max} \approx 11500$)].

Detection of phenol as a stable product of the reactions of MPC with pyridine and 4-aminopyridine at pH 6.9 was achieved through the 4-aminoantipyrine test.[9]

## Results

Second-order rate constants for nucleophilic attack of substituted pyridines on the substrates which are the subject of this work ($k_N$) were obtained as slopes of plots of eq 1, at constant pH and buffer concentration. In eq

$$k_{\text{obsd}} = k_0 + k_N[N]$$
$$k_0 = k_w + k_{OH}[OH^-] + k_B[B] \qquad (1)$$

1, N and B represent the free base forms of the substituted pyridine and phosphate buffer ($HPO_4^{2-}$), respectively, and $k_w$, $k_{OH}$, and $k_B$ are the rate constants for spontaneous hydrolysis and for the hydroxide and buffer reactions, respectively. The rate constant $k_B$ was obtained as the slope of plots of the latter part of eq 1 at various constant high pH values. The intercepts of these plots were replotted against hydroxide concentration in order to obtain $k_w$ and $k_{OH}$ as the new intercept and slope, respectively. The values of the rate constants obtained by this procedure and their standard errors are shown in Table III.

Jencks and Gilchrist have studied the reactions of 2,4-dinitrophenyl acetate (DNPA) with nicotinamide, pyridine, 4-methylpyridine, hydroxide ion, and water at 25 °C, ionic strength 1 M. The rate constants reported are 0.053, 2.5, and 13.0 $s^{-1}$ $M^{-1}$ respectively, for the substituted pyridines, and 54.0 and $2 \times 10^{-7}$ $s^{-1}$ $M^{-1}$ for the latter reactions.[1] These values satisfactorily agree with ours (Table III), taking into account the differences in ionic strength.

The nucleophilic character of the reactions of DNPA and methyl phenyl carbonate (MPC) with substituted pyridines was confirmed by their inhibition in the presence of added 2,4-dinitrophenolate and phenolate, respectively. This is caused by the back-reaction of the *N*-acetyl- or *N*-methoxycarbonylpyridinium ion intermediate with the corresponding phenolate.[1] The reactions of *p*-nitrophenyl methyl carbonate,[10] phenyl acetate, and *p*-nitrophenyl acetate[1] with pyridines and amines have also been shown to be nucleophilic.

Figure 1 shows the Brønsted plots obtained for the reactions of DNPA and MPC with substituted pyridines. The curve for DNPA was calculated from a semiempirical equation (eq 4) with $\beta_2 = 0.85$, $\beta_1 = 0.2$, p$K_a^\circ = 7.3$, and $\log k_N^\circ = 1.55$ (see Discussion).

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**Table I. Experimental Conditions for Determination of the Rate Constants and $k_{obsd}$ for the Nucleophilic Reactions of Substituted Pyridines and Phosphate Dianion with 2,4-Dinitrophenyl Acetate in Aqueous Solution at 25 °C (Unless Otherwise Noted), Ionic Strength 0.2 M[a]**

| nucleophile | concn of total nucleophile, M | pH | $k_{obsd}$,[b] $s^{-1}$ | no. of runs |
|---|---|---|---|---|
| 3-cyanopyridine[c] | 0.3-0.6 | 6.9 | $(3.3-5.0) \times 10^{-4}$ | 5 |
| | 0.3-0.6 | 7.2 | $(3.3-5.0) \times 10^{-4}$ | 5 |
| | 0.3-0.6 | 7.5 | $(3.3-5.1) \times 10^{-4}$ | 5 |
| 4-cyanopyridine[c] | 0.1-0.3 | 6.9 | $(3.9-9.2) \times 10^{-4}$ | 5 |
| | 0.1-0.3 | 7.2 | $(3.7-9.6) \times 10^{-4}$ | 5 |
| | 0.1-0.3 | 7.5 | $(3.9-9.8) \times 10^{-4}$ | 5 |
| 3-chloropyridine[c] | 0.02-0.1 | 6.9 | $(5.1-21.0) \times 10^{-4}$ | 6 |
| | 0.02-0.1 | 7.2 | $(5.4-22.4) \times 10^{-4}$ | 6 |
| | 0.02-0.1 | 7.5 | $(5.3-21.5) \times 10^{-4}$ | 6 |
| at 15 °C | 0.12-0.17 | 6.9 | $(1.1-1.6) \times 10^{-3}$ | 5 |
| at 35 °C | 0.05-0.12 | 7.5 | $(2.3-4.3) \times 10^{-3}$ | 5 |
| at 45 °C | 0.05-0.10 | 7.2 | $(4.4-7.5) \times 10^{-3}$ | 5 |
| nicotinamide[c] | 0.01-0.04 | 6.9 | $(5.4-19.1) \times 10^{-4}$ | 6 |
| | 0.01-0.04 | 7.2 | $(5.4-18.9) \times 10^{-4}$ | 6 |
| | 0.01-0.04 | 7.5 | $(5.3-19.2) \times 10^{-4}$ | 6 |
| pyridine[d] | 0.0035-0.01 | 4.9 | $(6.2-24.3) \times 10^{-4}$ | 6 |
| | 0.002-0.006 | 5.3 | $(9.8-27.9) \times 10^{-4}$ | 6 |
| | 0.0015-0.004 | 5.7 | $(14.2-42.3) \times 10^{-4}$ | 6 |
| 3-methylpyridine[d] | 0.0015-0.01 | 5.5 | $(6.3-79.0) \times 10^{-4}$ | 6 |
| | 0.002-0.01 | 5.8 | $(2.2-14.1) \times 10^{-3}$ | 6 |
| | 0.002-0.01 | 6.1 | $(1.5-20.1) \times 10^{-3}$ | 6 |
| 4-methylpyridine[d] | 0.0015-0.007 | 5.85 | $(6.0-24.4) \times 10^{-3}$ | 6 |
| | 0.0015-0.0045 | 6.15 | $(7.2-20.7) \times 10^{-3}$ | 6 |
| | 0.001-0.0035 | 6.45 | $(1.5-20.1) \times 10^{-3}$ | 6 |
| 4-aminopyridine[c] | 0.003-0.012 | 6.9 | $(2.5-10.4) \times 10^{-3}$ | 6 |
| | 0.0015-0.0065 | 7.2 | $(2.5-12.1) \times 10^{-3}$ | 6 |
| | 0.001-0.0035 | 7.5 | $(2.7-8.8) \times 10^{-3}$ | 6 |
| 4-dimethylaminopyridine[c] | 0.0015-0.005 | 6.9 | $(0.7-1.6) \times 10^{-3}$ | 6 |
| | 0.0015-0.005 | 7.2 | $(1.0-3.8) \times 10^{-3}$ | 6 |
| | 0.0015-0.005 | 7.5 | $(2.5-7.1) \times 10^{-3}$ | 6 |
| at 15 °C | 0.015-0.04 | 7.5 | $(7.8-24.4) \times 10^{-3}$ | 6 |
| at 35 °C | 0.001-0.0035 | 7.5 | $(2.7-8.4) \times 10^{-3}$ | 6 |
| at 45 °C | 0.001-0.0035 | 6.9 | $(1.9-4.7) \times 10^{-3}$ | 6 |
| phosphate dianion | 0.01-0.035 | 7.2 | $(0.5-1.3) \times 10^{-4}$ | 6 |
| | 0.04-0.08 | 7.7 | $(2.0-3.7) \times 10^{-4}$ | 5 |
| | 0.03-0.07 | 8.0 | $(2.5-4.2) \times 10^{-4}$ | 5 |
| | 0.04-0.06 | 8.3 | $(3.8-4.6) \times 10^{-4}$ | 5 |
| | 0.02-0.06 | 8.5 | $(2.7-5.1) \times 10^{-4}$ | 5 |

[a] Ionic strength maintained with sodium perchlorate. [b] Pseudo-first-order rate constant observed. In all cases the initial concentration of 2,4-dinitrophenyl acetate was $5 \times 10^{-6}$ M. [c] Reactions carried out in the presence of 0.01 M phosphate buffer. [d] Reactions carried out without external buffer.

**Table II. Experimental Conditions for Determination of the Rate Constants and $k_{obsd}$ for the Nucleophilic Reactions of Substituted Pyridines with Methyl Phenyl Carbonate in Aqueous Solution at 25 °C, Ionic Strength 0.2 M[a]**

| substituent | concn of total pyridine, M | pH | $k_{obsd}$,[b] $s^{-1}$ | no. of runs |
|---|---|---|---|---|
| none | 0.2-0.8 | 6.5 | $(2.3-2.9) \times 10^{-6}$ | 5 |
| | 0.2-0.8 | 7.5 | $(2.4-3.5) \times 10^{-6}$ | 5 |
| 3-methyl | 0.1-0.5 | 6.5 | $(1.7-5.0) \times 10^{-6}$ | 5 |
| | 0.1-0.5 | 7.5 | $(2.7-7.7) \times 10^{-6}$ | 5 |
| 4-methyl | 0.1-0.5 | 6.9 | $(5.0-13.8) \times 10^{-6}$ | 5 |
| | 0.1-0.5 | 7.2 | $(6.6-14.0) \times 10^{-6}$ | 5 |
| | 0.1-0.5 | 7.5 | $(7.8-15.4) \times 10^{-6}$ | 5 |
| 4-amino | 0.05-0.3 | 6.5 | $(1.7-7.9) \times 10^{-5}$ | 5 |
| | 0.05-0.3 | 7.5 | $(1.9-11.1) \times 10^{-4}$ | 5 |
| 4-dimethyl- | 0.02-0.07 | 6.7 | $(2.2-5.0) \times 10^{-5}$ | 5 |
| amino | 0.01-0.06 | 7.3 | $(2.0-12.7) \times 10^{-5}$ | 6 |

[a] Ionic strength maintained with potassium chloride. All reactions were carried out in the presence of 0.01 M phosphate buffer. [b] Pseudo-first-order rate constant observed. The initial concentration of methyl phenyl carbonate was $6 \times 10^{-4}$ M.

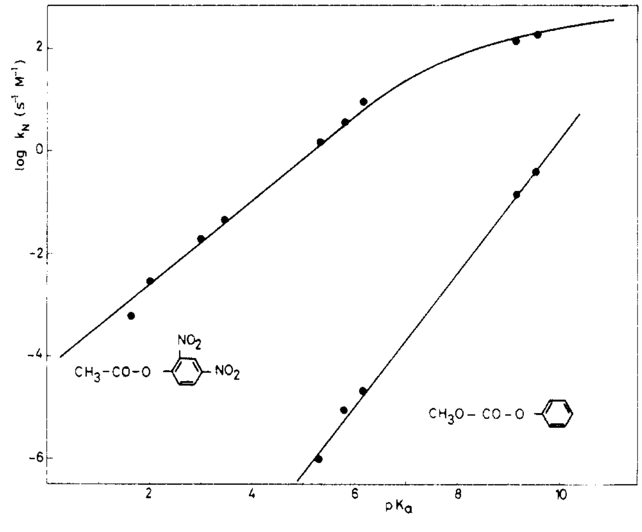


Figure 1. Logarithmic plot of the rate constants for the nucleophilic reactions of 2,4-dinitrophenyl acetate and methyl phenyl carbonate with substituted pyridines against their basicities at 25 °C, ionic strength 0.2 M. The line for the acetate was calculated from eq 4.

Activation parameters for the reactions of DNPA with two substituted pyridines (one on each side of the curvature of the Brønsted plot) were determined under the conditions shown in Table I. From values of $k_N$ obtained at four different temperatures (Table III), the following activation parameters were determined: $\Delta H^{\ddagger} = 11.2$ kcal $mol^{-1}$, $\Delta S^{\ddagger} = -28.5$ eu (3-chloropyridine), and $\Delta H^{\ddagger} = 10.6$

**Table III. Second-Order Rate Constants for the Reactions of Nucleophilic Reagents with 2,4-Dinitrophenyl Acetate (DNPA) and Methyl Phenyl Carbonate (MPC) in Aqueous Solution at 25 °C (Unless Otherwise Noted), Ionic Strength 0.2 M**

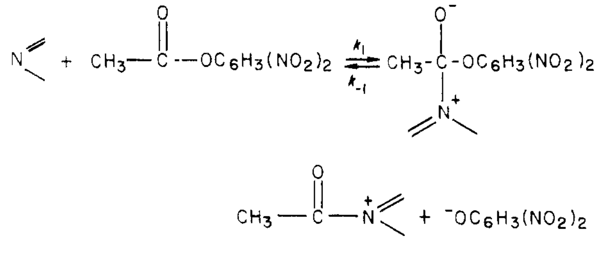
| | | $k$,[b] $M^{-1}\,s^{-1}$ | |
|---|---|---|---|
| nucleophile | $pK_a$[a] | DNPA | MPC |
| 3-cyanopyridine | 1.62 | $(5.8 \pm 0.3) \times 10^{-4}$ | |
| 4-cyanopyridine | 1.98 | $(2.8 \pm 0.2) \times 10^{-3}$ | |
| 3-chloropyridine | 2.98 | $(2.0 \pm 0.1) \times 10^{-2}$ | |
| at 15 °C | | $(0.9 \pm 0.1) \times 10^{-2}$ | |
| at 35 °C | | $(3.5 \pm 0.4) \times 10^{-2}$ | |
| at 45 °C | | $(6.4 \pm 0.5) \times 10^{-2}$ | |
| nicotinamide | 3.46 | $(4.5 \pm 0.2) \times 10^{-2}$ | |
| pyridine | 5.32 | $1.5 \pm 0.3$ | $(1.0 \pm 0.1) \times 10^{-6}$ |
| 3-methylpyridine | 5.81 | $3.5 \pm 0.3$ | $(8.8 \pm 0.5) \times 10^{-6}$ |
| 4-methylpyridine | 6.15 | $9.6 \pm 0.7$ | $(2.2 \pm 0.2) \times 10^{-5}$ |
| 4-aminopyridine | 9.15 | $143 \pm 14$ | $(1.5 \pm 0.2) \times 10^{-1}$ |
| 4-dimethylaminopyridine | 9.55 | $172 \pm 8$ | $(3.7 \pm 0.1) \times 10^{-1}$ |
| at 15 °C | | $75 \pm 8$ | |
| at 35 °C | | $275 \pm 30$ | |
| at 45 °C | | $490 \pm 40$ | |
| water | (−1.75) | $(1.8 \pm 0.1) \times 10^{-7}$ | |
| hydroxide anion | (15.75) | $60 \pm 6$ | |
| phosphate dianion | 6.77 | $(5.3 \pm 0.5) \times 10^{-3}$ | |

[a] Of the conjugate acid of the base at 25 °C, ionic strength 0.2 M, measured as previously described[5,19] (the figures for water and hydroxide are conventional). [b] The errors shown are standard errors of the slopes or intercepts obtained, by least-squares analysis, from plots of eq 1 (see text).

kcal mol$^{-1}$, $\Delta S^{\ddagger} = -12.8$ eu [4-(dimethylamino)pyridine].

## Discussion

The curved Brønsted plot obtained for the reactions of DNPA with a series of structurally similar substituted pyridines (Figure 1) can be interpreted in terms of a tetrahedral intermediate in the reaction path and a change in the rate-determining step (eq 2). Application of the



(2)

steady state treatment to the tetrahedral intermediate leads to eq 3, where $k_N$ is the overall rate constant for the

$$k_N = k_1k_2/(k_{-1} + k_2) \qquad (3)$$

nucleophilic attack. When the nucleophile is weakly basic (left side of the Brønsted plot), $k_{-1} \gg k_2$, and according to eq 3 $k_N = K_1k_2$, where $K_1$ is the equilibrium constant for the first step, and the second is the rate determining step. When the nucleophile is strongly basic (right side of the Brønsted plot), $k_{-1} \ll k_2$, $k_N = k_1$, and the first step is rate determining. Linear Brønsted relationships should result in both regions. For nucleophiles of intermediate basicities, eq 3 leads to a curve in this region of the Brønsted plot.

Taking into account the above considerations, a semiempirical equation has been deduced[5] (eq 4, where $\beta_1$ and

$$\log (k_N/k_N^{\circ}) = \beta_2(pK_a - pK_a^{\circ}) - \log \tfrac{1}{2}[1 + 10^{(\beta_2 - \beta_1)(pK_a - pK_a^{\circ})}] \qquad (4)$$

$\beta_2$ are the Brønsted slopes when the first and the second steps, respectively, are rate determining, and $k_N^{\circ}$ and $pK_a^{\circ}$ refer to the (hypothetical) nucleophile for which $k_{-1} = k_2$).

The line drawn for DNPA reactions in Figure 1 was calculated according to eq 4 with $\beta_1 = 0.2$, $\beta_2 = 0.85$, $pK_a^{\circ} = 7.3$, and $\log k_N^{\circ} = 1.55$. Although more experimental points are needed in the curved region, eq 4 seems to show a satisfactory fit to the experimental values of the rate constants. The value of $\beta_2$ agrees with the ones obtained for aminolysis reactions of reactive carbonyl compounds, such as 1-acetoxy-4-methoxypyridinium[1] ($\beta_2 = 0.8$), methyl chloroformate[5] ($\beta_2 = 0.93$), acetic anhydride[11] ($\beta_2 = 0.87$), 2,4-dinitrophenyl methyl carbonate[6] ($\beta_2 = 0.9$), phthalic and succinic anhydrides[12] ($\beta_2 = 0.8$), and nitrophenyl phenyl carbonates[4] ($\beta_2 = 1.0$). The value of $\beta_1$ also agrees with reported values of the Brønsted slope for this region.[4-6]

Our value of $pK_a^{\circ}$ is in accord with the one obtained for the reactions of 2,4-dinitrophenyl phenyl carbonate with quinuclidines[4] ($pK_a^{\circ} = 7.5$), and it is slightly lower than that obtained for the pyridinolysis reactions of 2,4-dinitrophenyl methyl carbonate[6] ($pK_a^{\circ} = 7.8$). The difference of these values illustrates the effect of the group that does not leave on the leaving ability of 2,4-dinitrophenolate from a tetrahedral intermediate relative to that of a tertiary amine. Our value for the difference between $pK_a^{\circ}$ and the $pK_a$ of 2,4-dinitrophenol at ionic strength 0.2 M[13] ($\Delta pK_a = 3.2$) is lower than that for 2,4-dinitrophenyl phenyl carbonate at ionic strength 1 M ($\Delta pK_a = 3.5$) and 2,4-dinitrophenyl methyl carbonate at ionic strength 0.2 M ($\Delta pK_a = 3.7$). Our result agrees with the conclusions of Gresser and Jencks[14] concerning the influence of the nonleaving group on partitioning of the tetrahedral intermediate; i.e., electron-donating groups will favor aryl oxide expulsion relative to amine. The situation is less clear when comparison is made between two carbonates in view of the larger electron-withdrawing ability of phenoxy than methoxy.

An interesting feature of the above pyridinolysis reactions is that DNPA has higher reactivity than 2,4-dinitrophenyl methyl carbonate[6] at $pK_a$ values lower than $pK_a^{\circ}$, and this is reversed at $pK_a$ values higher than $pK_a^{\circ}$. This behavior is clearly outside experimental error of the rate constants involved, and the reason for this is unknown.

The Brønsted plot obtained for the pyridinolysis reactions of MPC (Figure 1) is linear, and this is in agreement with the results achieved for the reactions of quinuclidines with substituted diphenyl carbonates.[4] According to these, $\Delta pK_a$ increases as the leaving aryl oxide group becomes more basic, and $\Delta pK_a \sim 7$ is expected for unsubstituted diphenyl carbonate, i.e., $pK_a^{\circ} \sim 17$. Therefore, the curvature of the Brønsted plot for MPC should be centered at $pK_a \sim 17$ (assuming similar behavior for substituted

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[11] A. R. Fersht and W. P. Jencks, *J. Am. Chem. Soc.*, **92**, 5432 (1970).

[12] W. E. Hall, T. Higuchi, I. H. Pitman, and K. Uekama, *J. Am. Chem. Soc.*, **94**, 8153 (1972).

[13] The $pK_a$ of 2,4-dinitrophenol at 25 °C, ionic strength 0.2 M (maintained with sodium perchlorate), was determined potentiometrically and gave a value of 4.1.

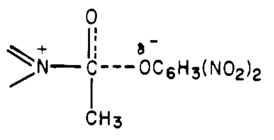
[14] M. J. Gresser and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 6970 (1977).

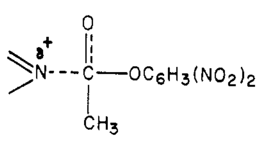
phenyl methyl carbonates), and this is far beyond the p$K_a$ range covered by substituted pyridines.

The Brønsted slope obtained for MPC (Figure 1) has a value of 1.3, which is higher than the values generally obtained for the corresponding slopes in aminolysis reactions of phenyl acetate[1] ($\beta = 1.0$) and other carbonyl compounds of similar reactivity[1,4,5] ($\beta = 0.9$–$1.0$). The higher $\beta$ value for MPC than for 2,4-dinitrophenyl methyl carbonate in the low p$K_a$ region[6] ($\beta_2 = 0.9$) in their reactions with substituted pyridines is consistent with a small increase in selectivity with decreasing reactivity over a wide range of reaction rates, according to Hammond[15] and other authors.[16]

The curved Brønsted plot of Figure 1 could also be described by assuming a one-step reaction and by using a treatment based on a change in transition-state geometry (a Hammond postulate[15] effect). This treatment has also been applied to the pyridinolysis reactions of methyl chloroformate,[17] but, as in the present case, the Brønsted curvature predicted is almost unnoticeable over the p$K_a$ range covered by the substituted pyridines.

The more negative value of $\Delta S^\ddagger$ obtained for the reaction of DNPA with 3-chloropyridine compared to that with 4-(dimethylamino)pyridine is in accord with the transition-state structures expected for rate-determining phenolate expulsion (I) and rate-determining pyridine attack (II), respectively. A change from rate-determining addition to rate-determining elimination has been reported to be accompanied by a large decrease of $\Delta S^\ddagger$ in nucleophilic vinylic substitution reactions.[18]


I


II

According to what has been discussed here and elsewhere,[4,14] the relative leaving abilities of oxygen and nitrogen bases from a tetrahedral intermediate depend not only on their nature but also on the nature of both the nonleaving group and other groups in the electrophilic reactant. We plan further work to study the influence of the group that does not leave on the relative leaving abilities of pyridines and phenolates for given systems.

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**Registry No.** 2,4-Dinitrophenyl acetate, 4232-27-3; 3-cyanopyridine, 100-54-9; 4-cyanopyridine, 100-48-1; 3-chloropyridine, 626-60-8; nicotinamide, 98-92-0; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 4-aminopyridine, 504-24-5; 4-(dimethylamino)pyridine, 1122-58-3; phosphate dianion, 14265-44-2; methyl phenyl carbonate, 13509-27-8; water, 7732-18-5; hydroxide ion, 14280-30-9.

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# Rates and Products of Addition of 4-Chlorobenzenesulfenyl Chloride to a Series of Methyl-Substituted 1,3-Butadienes[1]

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The rate and products of addition of 4-chlorobenzenesulfenyl chloride to 1,3-butadiene and 11 of its mono- and dimethyl derivatives have been determined in 1,1,2,2-tetrachloroethane at 25 °C. Substituting one of the hydrogens on 1,3-butadiene by a methyl group increases the rate of addition. The increase varies between 1.4 and 8.2 and depends upon the location of the methyl group relative to the double bond at which addition occurs. A slight preference for addition to the least substituted double bond is found. In general 1,2-adducts are formed in an anti-stereospecific manner. Upon standing the initial products isomerize to the 1,4-adducts in all cases except the adduct of addition to 1,3-butadiene. The results are consistent with a mechanism involving thiiranium ion like rate- and product-determining transition states.

Electrophilic additions to conjugated dienes are known to form products of 1,2 and 1,4 addition.[3] The proportions of these products and their stereochemistry have been determined for the reactions of numerous electrophiles with a number of different dienes. To our knowledge, however, no investigations have examined the effect of the structure of the conjugated diene upon the rate of electrophilic addition. We present some results on this neglected aspect of electrophilic additions to conjugated dienes.

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