sulting reaction mixture was then shaken with bicarbonate solution and water and the organic layer dried on $CaCl_2$. After evaporation of the toluene the residue was purified by chromatography on Al_2O_3 with hexane–toluene mixtures as eluents.

Pure **26** was isolated as an oil: mass spectrum,[27] m/e 282 (M^+, 36%), 191 (100), 165 (8), 91 (24); UV (EtOH) λ max (log ϵ), 283 nm (4.37); NMR ($CDCl_3$) δ 7.6–6.9 (m, 14 H, aromatic), 4.15 (br s, 2 H, H_{benzyl}, $J_{\text{homoallyl}}$ = 1 Hz), 3.87 ppm (br s, 2 H H(1)).

Registry No. (*E*)-**1**, 58719-65-6; *exo*-**2**, 58719-66-7; *endo*-**3**, 58769-73-6; **14**, 16275-02-8; **15**, 22495-71-2; **16**, 16275-01-7; **17**, 20669-52-7; **18**, 62019-39-0; **19**, 612-94-2; (*E,E*)-**22**, 27164-48-3; **25**, 100994-76-1; **26**, 18888-79-4; (*E,E*)-**28**, 33510-35-9; **29**, 38385-44-3; **30**, 38385-45-4.

[27] The peak at m/e 165 may be an indication that a small amount of 1-benzyl-1-phenyl-1*H*-indene is present as a side product. In the NMR spectrum and GLC no indication of this product could be observed.

Linear Free-Energy Relationship in the Pyridinolysis of 2,4-Dinitrophenyl *p*-Chlorobenzoate in Ethanol Aqueous Solution

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The title reactions are kinetically studied in 44 wt % aqueous ethanol at 25 °C, ionic strength 0.2 M (KCl). A linear Brönsted-type plot (log k_N against basicity of the substituted pyridine, where k_N is the second-order rate constant for the reactions) is found. The reactions are nucleophilic as shown by both the inhibition of the rate constant observed in the presence of added excess of 2,4-dinitrophenoxide ion and the value of the Brönsted-type slope (β 0.94). Comparison of the Brönsted-type obtained with those found in the pyridinolyses of 2,4-dinitrophenyl benzoate (curved, with the center of curvature at pK_a 9.5) and 2,4-dinitrophenyl *p*-nitrobenzoate (linear) under the same experimental conditions indicates that electron withdrawal from the remaining aryl group of the tetrahedral intermediate ($T^{\pm}$) formed in these reactions shifts the center of the Brönsted-type curvature toward higher pK_a values and hence favors amine expulsion from $T^{\pm}$ relative to 2,4-dinitrophenoxide ion. Activation parameters for the reactions of the title substrate with 3-methyl- and 4-(dimethylamino)pyridines are reported and their values discussed in comparison with the ones found for similar reactions.

Among the many types of free-energy relationships that have been applied to nucleophilic reactions of reactive carbonyl compounds the Brönsted-type equation is one which has received a good deal of attention.[1-9] When this equation applies to the reactions of a common substrate with a series of structurally homogeneous nucleophiles it takes the form log k_N = log G_N + βpK_a, where k_N is the rate constant for the nucleophilic reaction, K_a is the ionization constant of the conjugate acid of the nucleophile, and G_N and β are coefficients which depend on the substrate, the nucleophilic series, and the solvent.

In the reactions of a series of quinuclidines with aryl phenyl carbonates it has been found that the above equation is linear for the substrates with relatively poor leaving groups but becomes nonlinear as the leaving ability of these groups increases.[2a] Quantification of the Brönsted-type plots obtained shows that the value of the position of the center of the curvature on the pK_a axis (p$K_a°$) is smaller the larger the nucleofugality of the leaving group of the substrate.[2a] The same effect has been found in the reactions of a series of 3- and 4-monosubstituted pyridines with methoxycarbonyl and acetyl derivatives. The value of p$K_a°$ for the former reactions increases as the leaving group of the substrate changes from chloride (p$K_a°$ = 3.6)[3] to 2,4-dinitrophenoxide (p$K_a°$ = 7.8)[4] to *p*-nitrophenoxide,[5] and to phenoxide ions,[6] the two latter Brönsted-type plots being straight (p$K_a°$ > 10). Likewise, in the pyridinolysis of the acetyl substrates p$K_a°$ increases in the following series: acetyl chloride (p$K_a°$ = 3.6),[7] 2,4-dinitrophenyl acetate (p$K_a°$ = 7.3),[6] and *p*-nitrophenyl acetate (p$K_a°$ > 10).[3]

The effect of the nature of the nonleaving group of the substrate on the p$K_a°$ value has received less attention. Gresser and Jencks found that in the reactions of quinuclidines with aryl 3,4-dinitrophenyl carbonates the p$K_a°$ value increases as the "nonleaving" substituted phenoxy group becomes less basic (more electron-withdrawing).[2b] Similarly, in the pyridinolysis of 2,4-dinitrophenyl benzoates in aqueous ethanol the Brönsted-type plot found for the reactions of the *p*-nitrobenzoate derivative is straight,[8] whereas the same plot is curved for the unsubstituted substrate,[9] indicating that the p$K_a°$ value increases as the nonleaving group of the substrate is more electron-withdrawing.

In order to shed more light on the influence of the nature of the nonleaving group of the substrate on the p$K_a°$ value we continue in the present work our previous studies on

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Table I. Experimental Conditions and Values of k_{obsd} for the Reactions of 2,4-Dinitrophenyl *p*-Chlorobenzoate with Substituted Pyridines[a]

pyridine substituent	$10^2[N]_{tot}$,[b] M	F_N[c]	10^4k_{obsd}, s^{-1}	no. of runs
3-chloro	5.0–30.0	0.67	0.019–0.052	5
	5.0–60.0	0.80	0.023–0.105	9
	5.0–50.0	0.91	0.032–0.103	7
3-carbamoyl	4.0–38.0	0.50	0.023–0.155	10
	4.0–38.0	0.75	0.031–0.224	10
	4.0–38.0	0.90	0.033–0.274	10
none	4.0–40.0	0.50	1.22–9.20	10
	4.0–40.0	0.67	1.33–11.2	10
	4.0–40.0	0.83	1.79–14.5	10
3-methyl	3.0–30.0	0.33	1.38–9.99	10
	4.0–32.0	0.50	2.53–16.0	8
	1.8–18.0	0.67	1.18–11.2	11
at 15.5 °C	1.8–18.0	0.67	0.61–5.00	10
at 35.0 °C	1.8–18.0	0.67	2.49–22.2	10
at 45.0 °C	0.9–16.2	0.67	2.63–39.4	10
4-methyl	3.0–30.0	0.33	2.63–25.5	9
	1.5–27.0	0.50	2.02–34.8	10
	1.0–18.0	0.67	1.77–31.1	10
3,4-dimethyl	1.8–14.4	0.33	3.60–26.8	8
	1.0–10.0	0.50	2.94–29.8	10
	0.6–6.0	0.67	2.63–25.4	10
4-amino[d]	0.1–1.0	0.0028	1.34–15.8	9
	0.1–1.0	0.0053	3.01–28.2	10
	0.1–1.0	0.0158	8.50–83.9	10
4-dimethylamino[d]	0.2–2.0	0.0028	4.9–48.4	10
	0.1–1.0	0.0063	5.1–54.2	10
	0.1–1.0	0.0145	10.8–120	10
at 15.4 °C	0.1–1.0	0.0149	0.23–1.63	10
at 35.4 °C	0.1–1.0	0.0163	0.29–2.94	10
at 45.2 °C	0.1–1.0	0.0067	0.16–1.56	10

[a] In 44 wt % aqueous ethanol at 25 °C (unless otherwise stated) and ionic strength 0.2 M (maintained with potassium chloride). [b] Range of total concentration of the substituted pyridine (free-amine plus protonated forms). [c] Free amine fraction of total amine. $F_N = [N]/[N]_{tot}$, where N represents the free amine form. [d] These kinetics were carried out in the presence of phosphate ($H_2PO_4^-$ + HPO_4^{2-}) buffer. Total buffer concentration was 0.02 M.

the pyridinolysis of 2,4-dinitrophenyl benzoates[8,9] by choosing the reactions of the *p*-chlorobenzoate derivative. The value of the center of the Brönsted-type curve is important because it allows quantification of the relative leaving abilities of the nucleophile and leaving group from the tetrahedral intermediate formed in the reaction pathway.[2-9]

Experimental Section

Materials. The monosubstituted pyridines were purified as previously described,[3,6] and 3,4-dimethylpyridine was redistilled.[10] Analytical reagent grade disodium hydrogen phosphate and potassium chloride were used without further purification. Absolute analytical reagent grade ethanol and glass-distilled water were used throughout. Acetonitrile (solvent for the substrate stock solution) was distilled over phosphorus pentoxide.

2,4-Dinitrophenyl *p*-chlorobenzoate was prepared by combining equimolar amounts of 2,4-dinitrophenol and *p*-chlorobezoyl chloride, following the usual procedure.[11] It was identified by ^1H NMR and microanalysis, mp 148 °C (lit.[11] mp 145–147 °C).

Kinetic Measurements. The kinetics were studied by following the appearance of 2,4-dinitrophenol and/or its conjugate base at 320–360 nm by means of a Perkin-Elmer Lambda 3 spectrophotometer. The reactions were started by injection of stock solutions of the substrate in acetonitrile into the thermostated (±0.1 °C) kinetic solutions contained either in 1-cm cells, placed in the spectrophotometer (reactions with half-lives shorter than 2 h) or in flasks outside this instrument (reactions with half-lives greater than 7 h). In the latter cases aliquots (3 mL) were removed at appropriate time intervals and immediately analyzed spectrophotometrically. The concentration of acetonitrile in the solutions never exceeded 0.5%.

Table II. Experimental Conditions and k_{obsd} for the Reactions of 2,4-Dinitrophenyl *p*-Chlorobenzoate with 4-(Dimethylamino)pyridine in Excess of 2,4-Dinitrophenoxide Ion (DNP^-)[a-c]

$10^3[DNP^-]$, M	10^3k_{obsd}, s^{-1}	$10^3[DNP^-]$, M	10^3k_{obsd}, s^{-1}
0	2.30	2.78	1.78
0.48	2.26	3.81	1.70
1.44	1.96	4.36	1.56
1.93	1.86	4.72	1.50

[a] In 44 wt % aqueous ethanol at 25 °C and ionic strength 0.2 M (maintained with potassium chloride). [b] Total amine concentration 0.019 M, initial substrate concentration 5×10^{-5} M, pH 6.3. [c] The reactions were followed by means of a pH-stat (see Experimental Section).

The kinetics were measured under pseudo-order conditions, since the amine was in excess over the substrate. The initial substrate concentration was (0.5–2.0) × 10^{-4} M. The reactions were followed at least for three half-lives, and pseudo-first-order rate constants (k_{obsd}) were found from "infinity" plots. Those reactions showing correlation coefficients worse than 0.999 were rejected.

The experimental conditions of the reactions and the values of k_{obsd} are shown in Table I.

Kinetics in Excess of 2,4-Dinitrophenoxide Ion. The reaction of the substrate with 4-(dimethylamino)pyridine was studied under conditions of excess of 2,4-dinitrophenoxide ion (one of the reaction products) over the substrate. The aim was to test whether the reaction is nucleophilic (see Results). The experimental conditions for the reactions are shown in Table II.

These reactions were followed by potentiometric titration of the hydrogen ions released by means of a Radiometer pH-stat equipped with a PHM 62 pH meter, AUB 11 autoburet, TTT 60 titrator, REC 61 recorder provided with a REA 160 module, and a TTA 60 titration assembly. The electrodes were Radiometer G 2040 B (glass) and K 4040 (calomel). The titrant stored in the reservior of a 0.25-mL buret was an aqueous solution of 5×10^{-3} M sodium hydroxide, and the final volume of titrant added never exceeded 0.2 mL.

The reactions were started by injection of a stock solution of the substrate in acetonitrile (10 μL) into the thermostated kinetic solutions (10 mL) contained in the reaction vessel of the pH-stat. The substrate initial concentration was 5×10^{-5} M.

The reactions were followed for at least four half-lives. Pseudo-first-order rate constants (k_{obsd}) were found throughout. These were determined as the slopes of ln ($V_\infty - V$) vs. time plots, where V_∞ and V are the titrant volumes at infinity and variable times, respectively. The correlation coefficients obtained were better than 0.9995.

The values of k_{obsd} found for these reactions are shown in Table II.

Product Studies. 2,4-Dinitrophenoxide and *p*-chlorobenzoate ions were shown to be the only stable products of the reaction of the substrate with 4-(dimethylamino)pyridine, under the same experimental conditions as the kinetic runs (Table I). This conclusion was achieved by comparison of the final spectrum (200–500 nm) of the reaction solution with the corresponding one of an equimolar solution of 2,4-dinitrophenol and *p*-chlorobenzoic acid at the same conditons (pH 7.37).

The above analysis also showed that in the reactions of the substrate with nicotinamide under the kinetic conditions (Table I), 2,4-dinitrophenol and *p*-chlorobenzoic acid were the only stable products (pH 2.74).

Results

Under the experimental conditions of the kinetic measurements (Table I) the pseudo-first-order rate constant observed (k_{obsd}) for the pyridinolysis of 2,4-dinitrophenyl *p*-chlorobenzoate obeys eq 1, where k_o and k_N are rate

$$k_{obsd} = k_o + k_N F_N [N]_{tot} \qquad (1)$$

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Table III. Values of k_N Obtained in the Pyridinolysis of 2,4-Dinitrophenyl *p*-Chlorobenzoate and pK_a Values for the Substituted Pyridinium Ions[a]

pyridine substituent	pK_a[b]	k_N,[c] s^{-1} M^{-1}
3-chloro	2.17	$(1.9 \pm 0.2) \times 10^{-5}$
3-carbamoyl	2.67	$(7.7 \pm 0.7) \times 10^{-5}$
none	4.63	$(4.2 \pm 0.3) \times 10^{-3}$
3-methyl	4.92	$(9.4 \pm 0.6) \times 10^{-3}$
at 15.5 °C		$(4.1 \pm 0.3) \times 10^{-3}$
at 35.0 °C		$(1.8 \pm 0.1) \times 10^{-2}$
at 45.0 °C		$(3.7 \pm 0.2) \times 10^{-2}$
4-methyl	5.35	$(2.6 \pm 0.1) \times 10^{-2}$
3,4-dimethyl	5.68	$(6.0 \pm 0.3) \times 10^{-2}$
4-amino	8.98	56 ± 2
4-dimethylamino	9.14	87 ± 5
at 15.4 °C	9.52	69 ± 3
at 35.4 °C	8.79	109 ± 6
at 45.2 °C	8.49	138 ± 8

[a] Both pK_a and k_N were determined in 44 wt % aqueous ethanol at 25 °C (unless otherwise stated), ionic strength 0.2 M (maintained with potassium chloride). [b] From ref 9. The standard deviation is ±0.02. [c] Errors shown are standard deviations.

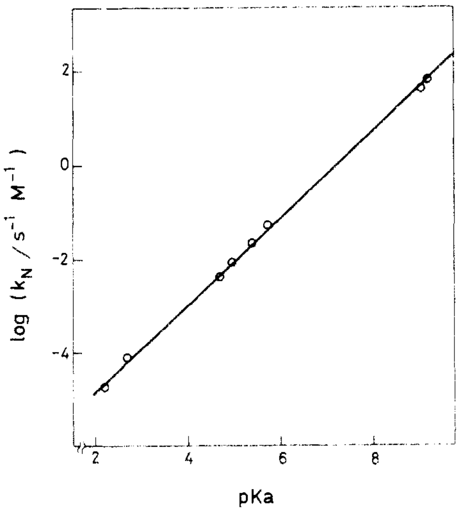


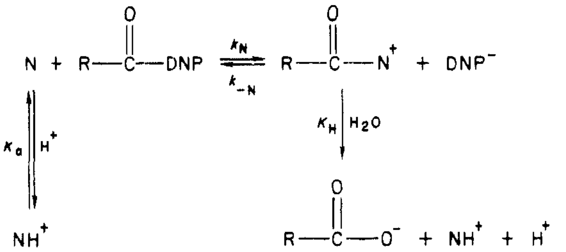
Figure 1. Brönsted-type plot obtained in the pyridinolysis of 2,4-dinitrophenyl *p*-chlorobenzoate in 44 wt % aqueous ethanol at 25 °C, ionic strength 0.2 M (KCl). The value of the slope (β) is 0.94.

constants for solvolysis and aminolysis, respectively, and F_N is the fraction of free amine ($F_N = [N]/[N]_{tot}$). The values of k_o and $k_N F_N$ were obtained as intercepts and slopes, respectively, of linear plots of k_{obsd} against $[N]_{tot}$ at constant F_N. The values of k_N were determined dividing by F_N the above values of the slopes. For most of the reactions k_o was negligible compared to the second term of eq 1. The most reliable value of k_o was found in the reactions of the substrate with 3-chloropyridine, the least reactive amine of the series studied. Under these reaction conditions (Table I) k_o did not show a dependence on F_N (i.e., pH), and the average value found was $(1.5 \pm 0.5) \times 10^{-6}$ s^{-1}.

The values of k_N did not exhibit variation with F_N, therefore, the final k_N values (shown in Table III) were obtained as an average of the values found at each F_N. The values of k_N were also obtained as the slopes of single linear plots of k_{obsd} against [N] (including the points for all the values of F_N). These agreed within 5% to the final k_N values shown in Table III.

The Brönsted-type plot for the reactions subject to the present study was drawn using the experimental pK_a values of the substituted pyridinium ions under the kinetic conditions and the final k_N values (both shown in Table III). The plot is linear (Figure 1) with slope $\beta = 0.94 \pm 0.03$ (r 0.9996).

Scheme I



3,4-Dimethylpyridine, the only disubstituted pyridine of the series in this study, correlates nicely with the monosubstituted analogues, as shown by the Brönsted-type plot of Figure 1. The same fact was found in the pyridinolyses of acetic acid,[1c] acetyl chloride,[7] phosphorylated 3-methyl- and 4-morpholinopyridines,[12] and 2,4-dinitrophenyl benzoate.[9]

Kinetics in Excess of 2,4-Dinitrophenoxide Ion. The reaction of the substrate with 4-(dimethylamino)pyridine was kinetically studied in excess of one of the products of the reactions, 2,4-dinitrophenoxide ion (DNP$^-$). The results and experimental conditions are shown in Table II. Under these conditions the mechanism for the reactions can be described by Scheme I, where R is *p*-chlorophenyl and N and NH$^+$ represent the free and protonated forms of 4-(dimethylamino)pyridine. Applying the "steady-state" approximation to the acylpyridinium derivative, eq 2 is obtained, where k_H includes the concentration of water.

$$k_{obsd} = \frac{k_N k_H [N]}{k_{-N}[DNP^-] + k_H} = \frac{k_N [N]}{(k_{-N}/k_H)[DNP^-] + 1} \qquad (2)$$

Inhibition of the reaction rate with the increase of DNP$^-$ is expected, therefore, if Scheme I (i.e., nucleophilic mechanism) is operative. A mechanism of general base catalysis would not lead to rate inhibition by increasing the concentration of DNP$^-$.[1a] Decrease of the rate constant with increasing concentration of the leaving group of the substrate has been found in the reactions of acetylimidazolium ion with acetate anion,[13] acetic anhydride with pyridine,[14] *p*-nitrophenyl and phenyl acetates with 4-methylpyridine,[1b] and phenyl methyl carbonate and 2,4-dinitrophenyl acetate with pyridine.[6] In all these cases inhibition of the rate constant has been attributed to nucleophilic catalysis.

Taking reciprocals of eq 2 yields eq 3. Since [N] is kept constant throughout the [DNP$^-$] variation, a plot of $1/k_{obsd}$ against [DNP$^-$] should be linear if Scheme I holds. Figure

$$\frac{1}{k_{obsd}} = \frac{1}{k_N[N]} + \frac{k_{-N}}{k_N k_H}[DNP^-] \qquad (3)$$

2 shows that this is the case for the present reaction. The curve of Figure 2A was calculated through eq 2 with the values $k_N[N] = 2.29 \times 10^{-3}$ s^{-1} and $(k_{-N}/k_H) = 105.2$ M^{-1}. These values were obtained from the intercept and slope, respectively, of a linear plot of eq 3 (shown in Figure 2B), by least-squares analysis. Since under the reaction conditions $[N] = 2.73 \times 10^{-5}$ M, it follows that $k_N = 83.9$ s^{-1} M^{-1}. This value is in good agreement with the one obtained in the reaction of the substrate with 4-(dimethylamino)pyridine with no added 2,4-dinitrophenoxide ion (Table III).

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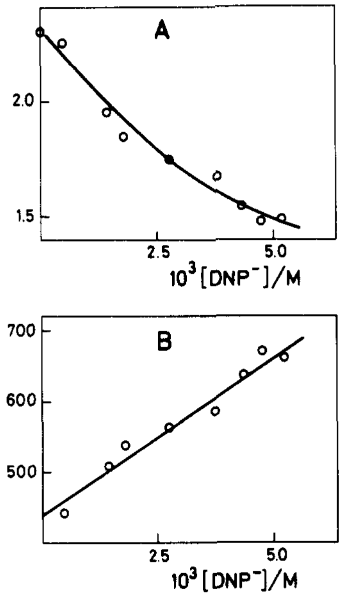


Figure 2. Rate inhibition of the reaction of 2,4-dinitrophenyl *p*-chlorobenzoate with 4-(dimethylamino)pyridine in added excess of 2,4-dinitrophenoxide ion (DNP^-). Experimental conditions as in Table II. The curve of plot A was calculated by means of eq 2 with the kinetic parameters obtained from plot B (see text).

The value of k_{-N}/k_H was obtained by multiplication of the slope of the plot in Figure 2B by k_N. The first-order rate constant k_H can be expressed as $k_H'[H_2O]$. Since at the experimental conditions of the reactions $[H_2O] = 27.8$ M, it follows that $k_{-N}/k_H' = 2.9 \times 10^3$. This is the second-order rate constants ratio for nucleophilic attack on the acylpyridinium ion intermediate by DNP^- and water (see Scheme I). It is difficult to find in the literature values of these rate constants ratios for the reactions of other substrates. Extrapolation to the pK_a of 2,4-dinitrophenol of the Brönsted-type plot obtained in the reactions of oxyanions with acetyl-4-methylpyridinium ion in aqueous solution at 25 °C, ionic strength 1 M, gives $k \approx 25\ s^{-1}\ M^{-1}$ for DNP^-.[1c] Dividing this value by $k = 0.0415\ s^{-1}\ M^{-1}$, the rate constant for hydrolysis of this substrate,[1c] yields $k_{DNP^-}/k_{H_2O} \approx 600$, which is smaller than the value for (*p*-chlorobenzoyl)-4-(dimethylamino)pyridinium ion. The difference of these values must arise from the dissimilar nature of the solvent and also from the different selectivity shown by these two substrates. It seems reasonable that the k_{DNP^-}/k_{H_2O} ratio for the acyl-4-(dimethylamino)pyridinium ion derivative be larger than the corresponding value for the 4-methylpyridinium ion analogue, in view of the lower reactivity of the former. For instance, the order of selectivities as measured by the rate constants ratio of phenoxide ion and water, k_{PhO^-}/k_{H_2O}, found for the reactions of acetylpyridinium, acetyl-4-methylpyridinium, and 1-(methoxycarbonyl)-4-(dimethylamino)pyridinium ions in aqueous solution at 25 °C is 10^{-8} (k_{PhO^-}/k_{H_2O}) = 1.36,[1c] 1.45,[1c] and 9.41,[15] respectively. There is a large increase in selectivity in going from the second to the third substrate in the series (a factor of ca. 6).

Discussion

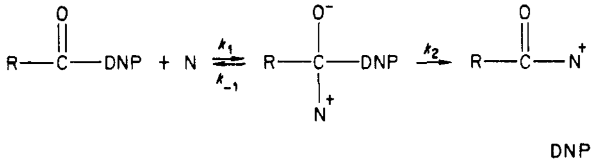
The value found for the Brönsted-type slope (β 0.94) and the inhibition shown by the reaction of the substrate with 4-(dimethylamino)pyridine show that all the reactions studied in the present work are nucleophilic.

The above straight plot is in contrast to the curved one obtained in the pyridinolysis of 2,4-dinitrophenyl benzoate (DNPB) in the same media.[9] Curvature was attributed to a tetrahedral intermediate in the reaction pathway and a change in the rate-determining step from the second to the first (eq 4, R phenyl) as the nucleophile becomes more basic. The Brönsted-type linearity found in the pyridinolyses of 2,4-dinitrophenyl *p*-chlorobenzoate (DNPCB, this work) and *p*-nitrobenzoate[8] (DNPNB) in the same media indicates that the second step of eq 4 is the rate-determining step for the reactions of all the substituted pyridines. This means that $k_{-1} \gg k_2$ (eq 4) even for the most basic pyridine of the series, confirming previous findings in reactions in aqueous solution that pyridines are better leaving groups than phenoxide ions of the same basicity.

Table IV. Values of the Activation Parameters Found for the Reactions of 2,4-Dinitrophenyl *p*-Chlorobenzoate (DNPCB) and Benzoate (DNPB) with 4-(Dimethylamino)- (DMAP) and 3-Methylpyridines (MP)[a]

reaction	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
DNPB + DMAP	2.3 ± 0.9	−44 ± 2
DNPCB + DMAP	3.6 ± 0.2	−38 ± 2
DNPB + MP	13 ± 1	−24 ± 2
DNPCB + MP	12.8 ± 0.8	−25 ± 2

[a] In 44 wt % Aqueous Ethanol, Ionic Strength 0.2 M (KCl). Errors shown are standard deviations.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-DNP + N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R-\underset{\underset{\displaystyle N^+}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-DNP \xrightarrow{k_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{+}{N} + DNP^- \quad (4)$$

The position of the center of the Brönsted curve on the pK_a axis (pK_a°) is important because a nucleophile of this pK_a value leaves as readily from the tetrahedral intermediate as the leaving group of the substrate, i.e., $k_{-1} = k_2$ in eq 4. The fact that $k_{-1} \gg k_2$ for the reactions of DNPCB and DNPNB with all the pyridines, means that pK_a° ≫ 9 (see Figure 1) for these reactions. Since the pyridinolysis of DNPB exhibits a curved Brönsted-type plot (pK_a° = 9.5)[9] it follows that pK_a° increases with the increase of the electron-withdrawing effect of the acyl moiety of the substrate. This was also found by Gresser and Jencks in the reactions of substituted quinuclidines with substituted aryl 3,4-dinitrophenyl carbonates in aqueous solution.[2b] The stronger the electron-withdrawing effect of the substituent on the aryl oxide moiety of the carbonate the higher the pK_a° value. This was attributed to greater stabilization of the transition state for 3,4-dinitrophenoxide ion expulsion relative to that for amine expulsion from the tetrahedral intermediate, as the nonleaving group becomes more electron-donating;[2b] i.e., k_2/k_{-1} of eq 4 increases (pK_a° decreases) with increasing electron donation from the nonleaving portion of the substrate.

Confirmation of the above findings is obtained by comparison of the Broönsted-type plots found in the pyridinolysis of 2,4-dinitrophenyl acetate[6] and 2,4-dinitrophenyl methyl carbonate[4] in aqueous solution. The latter reactions exhibit a larger pK_a° value (7.8 compared to 7.3) which can be attributed to the larger inductive electron-withdrawing effect from the tetrahedral intermediate of the methoxy group ($\sigma_I = +0.25$)[16] compared to that of methyl ($\sigma_I = -0.05$).[16] The electronic effects from groups attached to tetrahedral intermediates are mainly inductive, as discussed by Jencks and co-workers.[17]

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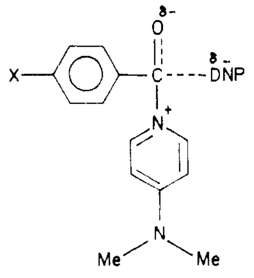
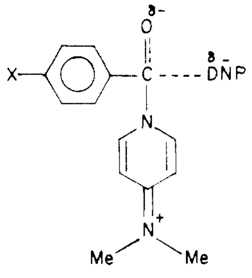
Activation Parameters. Table IV shows the activation parameters found for the reactions of DNPCB (this work) and DNPB[9] with two substituted pyridines. The large negative $\Delta S^{\ddagger}$ values for the reactions of 4-(dimethylamino)pyridine (DMAP) can be accounted for by assuming that I and II (X = H, Cl) are the two main canonical structures of the hybrid transition state of the second step of eq 4. Contribution of a canonical structure analogous to II to the ground-state DMAP should be smaller than the contribution of II to the hybrid transition state since the former involves total charge separation among the two nitrogen atoms. The loss of both rotational degrees of freedom and resonance in going from reactants to II, and the fact that the cationic amine nitrogen of II should be more solvated than the pyridine one of I (for steric reasons, due to the proximity of the latter to the acyl aryl group) explains the large negative $\Delta S^{\ddagger}$ values for the reactions of DMAP.[9]



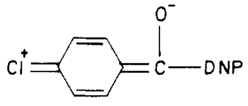
I



II

The reactions of DNPCB and DNPB with 3-methylpyridine (MP) show less negative $\Delta S^{\ddagger}$ values (Table IV) since with MP no contribution of structures similar to II are possible.

The lower (more negative) $\Delta S^{\ddagger}$ value found in the reaction of DMAP with DNPB compared to the reaction with DNPCB (Table IV) can be explained by the assumption that the canonical structure III contributes to the hybrid of DNPCB. The contribution of the analogous structure to the hybrid transition state for the DNPCB reaction should be smaller than in the ground state of DNPCB since it is known that the electronic effects of a group attached to a tetrahedral intermediate are mainly inductive.[17] Although the central carbon atom of the transition state is not exactly tetrahedral, the fact the tetrahedral intermediate involved in the reaction (eq 4) is very reactive implies that the above carbon atom has a strong tetrahedral character, according to the Hammond postulate.[18] The high polarity, and therefore large solvation (by polar solvents) of III, and the fact that a structure like III is negligible in the hybrid DNPB molecule, should be responsible for the higher (less negative) $\Delta S^{\ddagger}$ value found for the reaction of DNPCB.



III

The contribution of **II** to the hybrid transition state for the above reactions should be larger for X = Cl, in view of the value for the electron-withdrawing inductive effect of Cl ($\sigma_I = 0.47$),[16] which should favor that structure relative to I. This fact should lead to a higher $\Delta S^{\ddagger}$ for the reaction of DMAP with DNPB compared to that with DNPCB. The fact that $\Delta S^{\ddagger}$ is higher for the latter reaction (Table IV) means that the effect just mentioned is smaller than that discussed above regarding the contribution of III to the ground state of DNPCB.

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Registry No. 2,4-Dinitrophenyl p-chlorobenzoate, 32792-54-4; 3-chloropyridine, 626-60-8; 3-carbamoylpyridine, 98-92-0; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 3,4-dimethylpyridine, 583-58-4; 4-aminopyridine, 504-24-5; 4-(dimethylamino)pyridine, 1122-58-3.

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Reduction of Ketones by Tributyltin Hydride: The Effect of High Pressure on Steric Hindrance and Rearrangement Processes

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The reduction of sterically hindered ketones by tributyltin hydride under high pressure (1 GPa) afforded the corresponding alcohols in good yields without the need of free radical initiator or Lewis acid catalyst. Cyclopropyl ketones and α,β-epoxy ketones were also reduced in high yields under 1400 MPa with preservation of the three-membered ring.

The addition of tributyltin hydride to ketones is a well-known reaction that leads after protonolysis to the corresponding alcohols (Scheme I). A free radical mechanism is involved when the reaction is performed in the presence of azobisisobutyronitrile (AIBN), UV light, etc. Intermediate ionic species have to be considered when the addition is achieved in polar solvents or under Lewis acid catalysis.[1]

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