# Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 9.[1,2] *N*-Substituted 2,4,6-Triphenylpyridiniums, 5,6-Dihydro-2,4-diphenylbenzo[*h*]-quinoliniums, and 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c,h*]acridiniums: Kinetic Rate Variation with Structure of the *N*-Substituent

**Alan R. Katritzky,* Kumars Sakizadeh, Yu Xiang Ou, and Bratislav Jovanovic**
*School of Chemical Sciences, University of East Anglia, Norwich, and*
*Department of Chemistry, University of Florida, Gainesville, Florida 32611, U.S.A.*
**Giuseppe Musumarra,* Francesco P. Ballistreri, and Roberto Crupi**
*Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy*

*N*-n-Alkyl, *N*-s-alkyl, *N*-allyl, and *N*-benzyl derivatives of the title compounds react with piperidine and other nucleophiles in clearly separable $S_N1$ and/or $S_N2$ reactions. For *N*-s-alkyl compounds, $S_N2$ rates decrease with nucleophilicity of the nucleophile, whereas the $S_N1$ rates are unaffected by the nature of the nucleophile. The $S_N1$ reactions show higher activation entropies than found for the $S_N2$ reactions. Although for the same *N*-substituent, the $S_N2$ rate always increases in the order (1) < (2) < (3), the rate enhancement varies considerably for different *N*-substituents: the variations can be partially rationalized by the steric shape of the *N*-substituent. In general, as the *N*-substituent increases in size, the enhancement grows. For the $S_N2$ reactions, rates decrease in the order benzyl > methyl ≃ s-alkyl > continuous chain primary alkyl ≃ neopentyl. Comparisons with literature data involving other leaving groups, standardized by reference to the ethyl compound in each series, again show that groups larger than ethyl tend to react faster in series (1), (2), and especially (3) than expected, and methyl tends to react more slowly. Similar but smaller trends are found in literature data. Based on comparison of reactions of the corresponding benzyl compounds with thiourea and piperidine, the benzoquinoline leaving group is about as nucleofugic as chlorine, whereas the dibenzoacridine is considerably better than chlorine, though not quite as good as bromine.

Following our investigation of the steric[3] and electronic effects[4] of substitution in the pyridinium ring on nucleophilic displacements of *N*-benzylpyridiniums, we have now considered the rate dependence of such reactions on *N*-substituent structure. The biggest rate accelerations with the leaving group were found in the insertion of a $CH_2CH_2$ chain between the α-phenyl substituent and the β-position of the pyridinium ring;[3] we have therefore investigated a range of *N*-substituted benzoquinoliniums (2) and dibenzoacridiniums (3) for comparison with data on the parent 2,4,6-triphenylpyridiniums (1).

*Preparation of Compounds.*—Pyridiniums were prepared by standard methods from the corresponding pyryliums and appropriate primary amines:[5] details are given in Table 1.

*Kinetic Measurements.*—Reactions with piperidine, morpholine, and pyridine in chlorobenzene solutions were followed spectrophotometrically under pseudo-first-order conditions as previously described.[6] Observed rate constants were calculated from the slope of the plots of $\ln(\varepsilon_1 - \varepsilon_4)/(\varepsilon - \varepsilon_4)$ *versus* time for compounds in series (1) and from that of the plots of $\ln (D_0/D)$ *versus* time for compounds in series (2) and (3) (in these series $\varepsilon_4$ is zero). Such plots showed linearity to above 80% conversion in all cases with the following exceptions. (a) Compound (1m) exhibited curvature above 45% conversion; (b) compounds (2e, f, g, and n) exhibited curvature above 30% conversion; † (c) attempted kinetic runs for (1f and n) showed curvature throughout the plots, these reactions were extremely slow, and no rate constants could be obtained. Observed rate constants are recorded in Tables 2—5.

† Variations of substrate concentration have little effect on $k_2$ values for (2e and g) (see footnotes to Table 3).

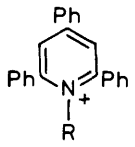
We have shown previously[3,6] that $k_{obs}$ for the reaction of 1-benzyl-2,4,6-triphenylpyridinium with piperidine is independent of the substrate concentration. This and similar independence now found for (2a) (*cf.* footnote *b* in Table 3) indicate that the different substrate concentrations adopted in the course of this work, to optimize absorbance variation during the kinetics, should not affect first- and second-order rate constants.

*Kinetic Results.*—As before, plots of the $k_{obs}$ against the nucleophile concentration generally gave straight lines which either passed through the origin or showed positive intercepts. The slopes are considered to vary as $k_2$, the second-order rate constants for $S_N2$ nucleophilic substitution; the intercepts are considered to vary as $k_1$, the first-order rate constants for $S_N1$ nucleophilic substitution (see Discussion in ref. 3). Changing the counterion from $BF_4^-$ to $ClO_4^-$ did not drastically affect measured $k_1$ and $k_2$ values in compound (2j).

The reactions of 2,4,6-triphenylpyridinium (1) with piperidine (Table 6) with *N*-(primary alkyl) groups showed small $k_2$ values ($3 \times 10^{-5}$—$60 \times 10^{-5}$ l mol$^{-1}$ s$^{-1}$) and insignificant $k_1$ values. For allyl $k_2$ is higher but $k_1$ remains insignificant. For the secondary alkyl groups, $k_2$ is also low ($2 \times 10^{-5}$—$15 \times 10^{-5}$) but $k_1$ is higher at $0.7 \times 10^{-5}$—$25 \times 10^{-5}$ s$^{-1}$.

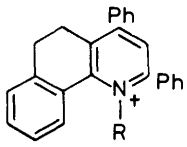
Second-order rates for the *N*-isopropyl- and *N*-s-butylpyridiniums with different nucleophiles decrease in the order piperidine > morpholine > pyridine, as already observed for the *N*-benzyl analogue,[6] while first-order rate constants [$0.9 \times 10^{-5}$ and $3 \times 10^{-5}$ for (1f and g), respectively] do not vary on changing the nucleophile.

For the tricyclic compounds (2) (Table 7), the $k_2$ values at 100 °C for primary alkyl groups (for Me $500 \times 10^{-5}$) and for other primary alkyls $10$—$100 \times 10^{-5}$ l mol$^{-1}$ s$^{-1}$) are significantly larger than those for the monocyclic analogues. The



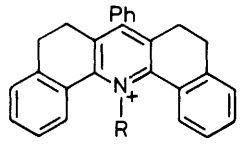
(1)

a; R = Me
b; R = Et
c; R = $Pr^n$
d; R = $Bu^n$
e; R = n-$C_5H_{11}$



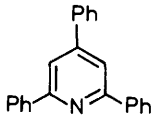
(2)

f; R = n-$C_6H_{13}$
g; R = n-$C_7H_{15}$
h; R = n-$C_8H_{17}$
i; R = $Pr^i$
j; R = $Bu^s$

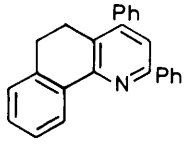


(3)

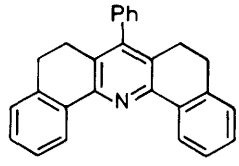
k; R = cyclo-$C_5H_9$
l; R = cyclo-$C_6H_{11}$
m; R = allyl
n; R = neo-$C_5H_{11}$
o; R = $CH_2Ph$
p; R = $CH_2CH_2Ph$



(4)



(5)



(6)

**Table 1.** Preparation of 1-substituted 2,4,6-triphenylpyridinium, 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium, and 14-substituted 5,6,8,9-tetrahydrodibenzo[*c*,*h*]acridinium perchlorates or tetrafluoroborates

| Compd. | Anion | Yield (%) | Cryst. solvent | M.p. (°C) | Crystal form | Found (%) C | H | N | Molecular formula | Required (%) C | H | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (1a) | *a* | 86 | EtOH | 216 | White plates | 68.2 | 4.8 | 3.3 | $C_{24}H_{20}NClO_4$ | 68.3 | 4.7 | 3.3 |
| (1b) | *a* | 75 | EtOH | 124 | White needles | 68.8 | 5.1 | 3.1 | $C_{25}H_{22}NClO_4$ | 68.9 | 5.1 | 3.2 |
| (1f) | *a* | 77 | EtOH | 248 | White needles | 70.2 | 5.9 | 3.0 | $C_{29}H_{30}NClO_4$ | 70.8 | 6.1 | 2.9 |
| (1i) | *a* | 80 | EtOH | 204 | White needles | 69.1 | 5.3 | 2.9 | $C_{26}H_{25}NClO_4$ | 69.3 | 5.6 | 3.1 |
| (1l) | *a* | 83 | EtOH | 188 | White needles | 70.9 | 5.9 | 2.8 | $C_{29}H_{28}NClO_4$ | 71.1 | 5.7 | 2.9 |
| (1m) | *a* | 89 | EtOH | 112 | White needles | 69.7 | 4.9 | 3.0 | $C_{26}H_{22}NClO_4$ | 69.7 | 4.9 | 3.1 |
| (2a) | *b* | 71 | $Pr^iOH$ | 132 | Yellow needles | 71.3 | 5.1 | 3.3 | $C_{26}H_{22}NBF_4$ | 71.8 | 5.1 | 3.2 |
| (2b) | *b* | 84 | $Pr^iOH$ | 122 | Yellow needles | 72.3 | 5.3 | 3.2 | $C_{27}H_{24}NBF_4$ | 72.2 | 5.4 | 3.1 |
| (2c) | *b* | 87 | $Me_2CO$–$Et_2O$ | 158 | Yellow plates | 72.4 | 5.6 | 3.0 | $C_{28}H_{26}NBF_4$ | 72.5 | 5.6 | 3.0 |
| (2e) | *b* | 81 | $Me_2CO$–$Et_2O$ | 100 | Yellow plates | 73.1 | 6.1 | 2.8 | $C_{30}H_{30}NBF_4$ | 73.3 | 6.1 | 2.8 |
| (2f) | *a* | 70 | EtOH | 159—160 | White needles | | | | $C_{31}H_{32}NClO_4$ | 71.9 | 6.2 | 2.7 |
| (2g) | *b* | 76 | $Me_2CO$–$Et_2O$ | 85 | Yellow plates | 71.5 | 6.8 | 2.6 | $C_{32}H_{34}NBF_4 \cdot H_2O$ | 71.5 | 6.7 | 2.6 |
| (2m) | *b* | 76 | EtOH | 164 | White needles | 72.9 | 5.1 | 3.2 | $C_{28}H_{24}NBF_4$ | 72.9 | 5.2 | 3.0 |
| (2n) [c] | *b* | 61 | $Me_2CO$–$Et_2O$ | 227—229 | Yellow needles | 73.2 | 6.2 | 2.8 | $C_{30}H_{30}NBF_4$ | 73.3 | 6.1 | 2.9 |
| (3c) | *b* | 79 | $Me_2CO$–$Et_2O$ | 213 | Green plates | 73.4 | 5.8 | 2.8 | $C_{30}H_{28}NBF_4$ | 73.6 | 5.7 | 2.8 |
| (3e) | *b* | 74 | $Me_2CO$–$Et_2O$ | 118 | Green plates | | *d* | | $C_{32}H_{32}NBF_4$ | | | |

[a] Perchlorate. [b] Tetrafluoroborate. [c] Reported in ref. 17 as a perchlorate, m.p. 229—231 °C. [d] Characterised by mass spectrum: $C_{32}H_{32}N^+$ requires 430.2535; found 430.2535. $C_{32}H_{32}N^+ - C_5H_{11} = C_{27}H_{21}N^+$ requires 359.1674; found 359.1673.

$k_1$ values for primary alkyl groups are significant for the n-pentyl, n-hexyl, and n-heptyl derivatives where they vary from 0.6 to $10^{-5}$ to $5 \times 10^{-5}$ $s^{-1}$. For the secondary alkyl tricyclics, $k_2$ is $300 \times 10^{-5}$—$800 \times 10^{-5}$ l $mol^{-1}$ $s^{-1}$ with $k_1$ at $100 \times 10^{-5}$—$350 \times 10^{-5}$ $s^{-1}$; however, the rates for the $Pr^i$ (2i) and $Bu^s$ (2j) compounds were difficult to measure accurately at 100°; at this temperature reproducibility fell off although at lower temperatures $k_{obs}$ could be reproduced with 5% consistency. Neopentyl showed an appreciable $k_2$ value.

For the pentacyclic derivatives (3) (Table 8), $k_2$ is $200 \times 10^{-5}$—$2\,500 \times 10^{-5}$ l $mol^{-1}$ $s^{-1}$ for primary alkyl groups.

Activations parameters for both uni- and bi-molecular reactions are recorded in Table 9.

In chlorobenzene at 120 °C, the dibenzoacridiniums (3c, g, and p) underwent elimination of the *N*-n-alkyl substituent at rates independent of the concentration of 2,4,6-triphenylpyridine present (Table 10). Rates for the *N*-n-heptyl derivative (3g) at 100 °C with various nucleophiles (Table 8) show a decrease in second-order rate constant ($k_2$); it is probable that there is an increase in the percentage reaction by the $S_N1$ route as nucleophile strength decreases, but the $k_1$ value remains uncertain.

*Dependence of Second-order Rates on Variation of Nucleophile.*—The second-order rates for the reactions of *N*-s-alkyl monocyclic pyridiniums (1i and j) with morpholine and pyridine are lower than those for piperidine, increasing in the order: pyridine < morpholine < piperidine. With pyridine, $k_2$ values are affected by large errors; clearly the reaction proceeds almost entirely by the $S_N1$ process with this nucleophile.

*Dependence of Second-order Rates* $k_2$ *with Piperidine as Nucleophile on Leaving Group* (*Table* 11).—For benzyl, we

**Table 2.** Pseudo-first-order rate constants ($k_{obs}$) for the reactions of 1-substituted 2,4,6-triphenylpyridinium cations with piperidine, morpholine, and pyridine in chlorobenzene at 100 °C

| Compound | Nucleophile | [Nu]/mol $l^{-1}$ | $10^5k_{obs}/s^{-1}$ | Compound | Nucleophile | [Nu]/mol $l^{-1}$ | $10^5k_{obs}/s^{-1}$ |
|---|---|---|---|---|---|---|---|
| (1b) [a] | piperidine | 0.480 | 1.45 | (1k) [a] | piperidine | 0.320 | 30.0 |
| | | 0.320 | 0.948 | | | 0.160 | 28.0 |
| | | 0.240 | 0.714 | | | 0.080 | 26.4 |
| | | 0.160 | 0.471 | | | 0.0320 | 25.9 |
| (1i) | morpholine | 0.240 [a] | 2.44 | (1l) [a] | piperidine | 0.320 | 3.75 |
| | | 0.160 [a] | 1.89 | | | 0.160 | 3.40 |
| | | 0.080 [a] | 1.36 | | | 0.080 | 3.28 |
| | | 0.001 60 [c] | 0.927 | | | 0.0320 | 3.16 |
| | pyridine [a] | 0.960 | 1.57 | | | | |
| | | 0.640 | 1.33 | (1m) [b] | piperidine | 0.320 [a] | 31.0 |
| | | 0.320 | 1.16 | | | 0.240 [a] | 25.2 |
| | | | | | | 0.160 [a] | 20.2 |
| (1j) | morpholine | 0.320 [a] | 4.59 | | | 0.0800 [a] | 8.83 |
| | | 0.160 [a] | 3.80 | | | 0.0400 [c] | 6.23 |
| | | 0.080 [a] | 3.35 | | | 0.008 00 [c] | 1.63 |
| | | 0.0320 [c] | 3.08 | | | 0.001 60 [c] | 0.642 |
| | pyridine [a] | 0.480 | 3.16 | | | | |
| | | 0.320 | 3.12 | | | | |
| | | 0.160 | 3.05 | | | | |

[a] Concentration of pyridinium $1.60 \times 10^{-3}$ mol $l^{-1}$. [b] Kinetics were followed up to 45% conversion, above which curvature of the plot of $\ln[(\varepsilon_1 - \varepsilon_4)/(\varepsilon - \varepsilon_4)]$ *versus* time was observed. [c] Concentration of pyridinium $3.20 \times 10^{-5}$ mol $l^{-1}$.

**Table 3.** Pseudo-first-order rate constants ($k_{obs}$) for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cations with piperidine in chlorobenzene at 100 °C

| Compound | [Nu]/mol $l^{-1}$ | $10^5k_{obs}/s^{-1}$ | Compound | [Nu]/mol $l^{-1}$ | $10^5k_{obs}/s^{-1}$ | Compound | [Nu]/mol $l^{-1}$ | $10^5k_{obs}/s^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| (2a) [a] | 0.320 | 168 | (2e) [a,c] | 0.400 | 8.23 | (2j) | 0.0240 [a,h] | 368 |
| | 0.256 | 123 | | 0.320 [d] | 7.03 | | 0.0160 [a,h] | 364 |
| | 0.160 [b] | 82.9 | | 0.240 | 5.93 | | 0.009 60 [i,j] | 350 |
| | 0.0960 | 52.0 | | 0.160 | 4.85 | | 0.008 00 [a,j] | 335 |
| | | | | | | | 0.004 80 [a,j] | 342 |
| (2b) [a] | 0.160 | 21.2 | (2f) [c,e] | 0.320 | 3.75 | | 0.002 40 [i,j] | 336 |
| | 0.0800 | 9.72 | | 0.160 | 2.17 | | 0.000 800 [a,j] | 329 |
| | 0.0320 | 4.20 | | 0.120 | 1.80 | | 0.0320 | 156 |
| | 0.0160 | 2.19 | | | 1.41 | | | |
| | | | | | | (2m) [a] | 0.0160 | 84.4 |
| (2c) [a] | 0.320 | 15.6 | (2g) [a,c] | | 8.83 | | 0.0120 | 60.6 |
| | 0.240 | 11.8 | | 0.320 [f] | 7.93 | | 0.008 00 | 45.3 |
| | 0.160 | 7.77 | | 0.240 | 7.21 | | | |
| | 0.0800 | 3.87 | | 0.160 | 6.24 | (2n) [a,c] | 0.400 | 4.79 |
| | | | | | | | 0.320 | 4.37 |
| (2d) [a] | 0.320 | 22.6 | (2i) [g] | 0.320 | 201 | | 0.240 | 3.50 |
| | 0.256 | 18.5 | | 0.240 | 177 | | 0.160 | 2.07 |
| | 0.0640 | 5.00 | | 0.160 | 156 | | 0.0800 | 0.750 |
| | | | | 0.0800 | 134 | | | |

[a] Concentration of pyridinium $6.40 \times 10^{-5}$ mol $l^{-1}$. [b] Kinetic runs at concentration of pyridinium $1.60 \times 10^{-3}$ and $4.00 \times 10^{-4}$ mol $l^{-1}$ gave $10^5k_{obs}$ 78.5 and 78.0 $s^{-1}$ respectively. [c] Kinetics followed up to 30% conversion above which curvature of the plot of $\ln(D_0/D)$ *versus* time was observed. [d] A kinetic run at concentration of pyridinium $3.20 \times 10^{-5}$ mol $l^{-1}$ gave $10^5k_{obs}$ 6.93 $s^{-1}$. [e] Concentration of pyridinium $6.40 \times 10^{-4}$ mol $l^{-1}$. [f] A kinetic run at concentration of pyridinium $3.20 \times 10^{-5}$ mol $l^{-1}$ gave $10^5k_{obs}$ 8.24 $s^{-1}$. [g] Concentration of pyridinium $1.60 \times 10^{-3}$ mol $l^{-1}$. [h] $ClO_4^-$ salt. [i] Concentration of pyridinium $9.60 \times 10^{-5}$ mol $l^{-1}$. [j] $BF_4^-$ salt

found earlier [2] that the use of tricyclic or pentacyclic leaving groups produced large rate enhancements, respectively faster by *ca.* 69 and 900 times, compared with the 2,4,6-triphenylpyridinium analogue. We now see that these rate enhancements can vary widely for other groups. Thus allyl shows enhancements of 48 and 58, methyl of 8 and 42, whereas ethyl displays 43 and 220. These enhancement factors appear to be related to the overall steric requirements of the *N*-substituent. Thus allyl and ethyl both respond much more than methyl to the change from (1) to (2), but methyl and ethyl respond much more than allyl to the second annulation involved in going from (2) to (3). A much higher rate increase (up to 30 times) due to the second annulation is found for n-pentyl, n-hexyl, and n-heptyl groups [comparisons of relative rates for these three groups are tentative as the kinetics for (2e—g) were not followed to complete conversion, see footnote *d* in Table 11]. The biggest enhancements are found for benzyl. Thus, the enhancement in rate for primary alkyl groups tends to increase with the bulk of the alkyl group.

For the secondary alkyl groups, the effect of annulation is greater for s-butyl than isopropyl. Stable pentacyclic compounds of series (3) cannot be prepared with secondary alkyl *N*-substituents, because of spontaneous fast $S_N1$ reactions.[7]

*First-order Rates.*—In the monocyclic series (1) and the pentacyclic series (3), the first-order rates for primary alkyl groups were not significant (see Tables 6 and 8). For the higher *N*-n-alkyl compounds of the tricyclic series, apparently significant first-order rates are determined (Table 7), but these could well be artifacts arising from the inherent curvature of the kinetic plots for the compounds concerned (see footnote *e* of Table 7).

For the *N*-secondary alkyl compounds, first-order rate constants in the monocyclic series (1) increase in the order: isopropyl < cyclohexyl < s-butyl < cyclopentyl; in the tricyclic series (2), the two available results show the reactivity sequence: isopropyl < s-butyl (Table 12). Order of magnitude calculations based on the spontaneous $S_N1$ reactions found [7] to occur when the pentacyclic pyrylium reacts with s-alkyl primary amines indicate that $k_1$ in the pentacyclic series (3) for s-alkyl groups is $\geqslant 5\ s^{-1}$ at 100 °C. This implies rate enhancements of at least 20 000 as compared to series (1) and of at least 1 000 as compared with series (2).

First-order rates for the *N*-isopropyl and *N*-s-butyl compounds (1i and j) do not change appreciably on changing the nucleophile from piperidine to morpholine or pyridine (Table 6). This invariance, already observed for the *N*-*p*-methoxybenzyl compound [8] can, in our opinion, be interpreted as evidence that there is no merging of the $S_N1$ and $S_N2$ mechanisms, but that both mechanisms proceed independently.

*Comparison of Leaving Group Nucleofugacity with that of Halogens.*—We have previously shown [2b,3] that steric acceleration causes rate increases in series (2) and (3) in comparison to series (1). To compare the leaving group capability of pyridiniums of series (2) and (3) with that of familiar leaving groups such as the halogens, we determined the second-order rate constants for the reaction of *N*-benzylpyridiniums (2o) and (3o) with thiourea in MeOH at 35 °C. These results are summarized in Table 13.

While the monocyclic derivative (1o) reacted too slowly under the conditions used, the tricyclic (2o) and pentacyclic (3o) compounds exhibited second-order rates which are respectively 600 and 15 times lower than of benzyl bromide (*cf.* Table 13). This absolute comparison of the reactivity of (3o) with that of benzyl bromide shows clearly the pentacyclic pyridinium to be a leaving group somewhat poorer than bromide.

**Table 4.** Pseudo-first-order rate constants ($10^5 k_{obs}/s^{-1}$) for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cations with piperidine in chlorobenzene at various temperatures [a]

| Compd. | [Pip]/mol $l^{-1}$: / *t*/°C | 0.08 | 0.16 | 0.24 | 0.32 | 0.40 |
|---|---|---|---|---|---|---|
| (2a) | 60 | | 3.39 | 4.68 | 6.30 | 7.74 |
| | 70 | 3.57 | 7.50 | 12.2 | 16.1 | |
| | 80 | 11.0 | 17.4 | 27.0 | 37.0 | |
| (2i) | 50 | | 2.47 | 3.59 | 4.44 | 5.56 |
| | 60 | 3.82 | 6.42 | 8.71 | 10.9 | |
| | 83 | 34.2 | 50.2 | 63.1 | 74.1 | |
| (2j) | 60 | 5.46 | 7.58 | 9.91 | 12.3 | |
| | 70 | 21.3 | 27.5 | 33.6 | 39.0 | |
| | 81 | 69.1 | 105 | 121 | 150 | |

[a] Concentration of quinolinium cation $6.4 \times 10^{-4}$ mol $l^{-1}$.

**Table 5.** Pseudo-first-order rate constants ($k_{obs}$) for the reactions of 14-substituted 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium cations with nucleophiles in chlorobenzene

| Compound | Nucleophile (*t*/°C) | [Nu]/mol $l^{-1}$ | $10^5 k_{obs}/s^{-1}$ |
|---|---|---|---|
| (3a) [a] | Piperidine (100) | 0.128 | 331 |
| | | 0.0960 | 219 |
| | | 0.0640 | 145 |
| | | 0.0320 | 87.2 |
| | | 0.006 40 | 14.0 |
| (3b) [b] | Piperidine (100) | 0.200 | 140 |
| | | 0.160 | 113 |
| | | 0.0800 | 57.2 |
| | | 0.0320 | 28.4 |
| (3c) [a] | Piperidine (100) | 0.160 | 43.8 |
| | | 0.0800 | 21.9 |
| | | 0.0320 | 8.61 |
| (3d) [a] | Piperidine (100) | 0.320 | 82.1 |
| | | 0.250 | 65.7 |
| | | 0.190 | 50.8 |
| (3e) [a] | Piperidine (100) | 0.240 | 47.6 |
| | | 0.160 | 32.0 |
| | | 0.0800 | 16.0 |
| | | 0.0320 | 6.25 |
| (3f) [b] | Piperidine (100) | 0.240 | 73.5 |
| | | 0.160 | 46.5 |
| | | 0.080 | 24.2 |
| | | 0.0320 | 9.53 |
| (3g) [c] | Piperidine (95) | 0.160 | 28.6 [d,e] |
| | Piperidine (100) | 0.480 | 121 |
| | | 0.320 | 81.0 |
| | | 0.160 | 40.8 |
| | Piperidine (110) | 0.16 | 72.1 [e,f] |
| | Pyridine (100) | 1.28 | 2.03 |
| | | 0.640 | 1.23 |
| | | 0.320 | 0.756 |
| | Morpholine (100) | 1.28 | 101 |
| | | 0.960 | 81.6 |
| | | 0.640 | 57.3 |
| | | 0.480 | 41.2 |
| (3m) [a] | Piperidine (100) | 0.0640 | 369 |
| | | 0.0160 | 87.4 |
| | | 0.0120 | 73.6 |
| | | 0.008 00 | 52.9 |
| | | 0.004 00 | 38.4 |

[a] Concentration of pyridinium $6.40 \times 10^{-5}$ mol $l^{-1}$. [b] Concentration of pyridinium $9.70 \times 10^{-5}$ mol $l^{-1}$. [c] Substrate concentration $1.60 \times 10^{-3}$ mol $l^{-1}$. [d] $k_2$ $1.79 \times 10^{-3}$ l $mol^{-1}$ $s^{-1}$. [e] $k_2$ Obtained from $k_{obs}$/[Nu]; this compound reacts exclusively by the $S_N2$ mechanism. [f] $k_2$ $4.51 \times 10^{-3}$ l $mol^{-1}$ $s^{-1}$.

**Table 6.** First-order ($k_1$) and second-order ($k_2$) rate constants for the reaction of 2,4,6-triphenyl-1-(substituted benzyl)pyridinium cations with piperidine, morpholine, and pyridine in chlorobenzene at 100 °C

| Compound | Nucleophile | $N$ [a] | $r$ [b] | Slope | | Intercept | | $\frac{10^3k_1}{k_2 + 10k_1}$ [d] |
|---|---|---|---|---|---|---|---|---|
| | | | | $10^3k_2$/l mol$^{-1}$ s$^{-1}$ [c] | % Error | $10^5k_1$/s$^{-1}$ [c] | % Error | |
| (1a) [e] | Piperidine | 4 | 0.9996 | 0.600 ± 0.034 | 6 | (−0.4 ± 0.9) | | <7 |
| (1b) | Piperidine | 4 | 0.9998 | 0.0306 ± 0.0009 | 3 | (−0.02 ± 0.3) | | <3 |
| (1i) [e] | Piperidine | 5 | 0.999 | 0.140 ± 0.005 | 4 | 0.72 ± 0.21 | 29 | 34 |
| | Morpholine | 4 | 0.999 | 0.064 ± 0.007 | 10 | 0.88 ± 0.10 | 11 | 61 |
| | Pyridine | 3 | 0.995 | 0.006 ± 0.004 | 67 | 0.94 ± 0.29 | 30 | >99 |
| (1j) [e] | Piperidine | 5 | 0.993 | 0.11 ± 0.02 | 16 | 3.2 ± 0.5 | 15 | 74 |
| | Morpholine | 4 | 0.999 | 0.052 ± 0.004 | 7 | 2.9 ± 0.07 | 2 | 85 |
| | Pyridine | 3 | 0.988 | (0.003 ± 0.003) | | 3.0 ± 0.1 | 4 | >99 |
| (1k) | Piperidine | 4 | 0.995 | 0.15 ± 0.03 | 20 | 25.4 ± 0.6 | 2 | 94 |
| (1l) | Piperidine | 4 | 0.998 | 0.020 ± 0.003 | 14 | 3.10 ± 0.05 | 2 | 94 |
| (1m) [f] | Piperidine | 7 | 0.991 | 0.97 ± 0.11 | 11 | (1.6 ± 1.9) | | <27 |

[a] Number of runs. [b] Correlation coefficient. [c] 90% confidence limits. [d] *i.e.* % reaction by $S_N1$ route at [piperidine] $10^{-1}$ mol l$^{-1}$. [e] Values from G. Musumarra, F. P. Ballistreri, S. Muratore, A. R. Katritzky, and S. Wold, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1049. [f] Kinetics were followed up to 45% conversion.

**Table 7.** First-order ($k_1$) and second-order ($k_2$) rate constants for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cations with piperidine in chlorobenzene

| Compound | $t$/°C | $N$ [a] | $r$ [b] | Slope | | Intercept | | $\frac{10^3k_1}{k_2 + 10k_1}$ [d] |
|---|---|---|---|---|---|---|---|---|
| | | | | $10^3k_2$/l mol$^{-1}$ s$^{-1}$ [c] | % Error | $10^5k_1$/s$^{-1}$ [c] | % Error | |
| (2a) | 60 | 4 | 0.999 | 0.183 ± 0.016 | 9 | (0.4 ± 0.5) | | <30 |
| | 70 | 4 | 0.999 | 0.53 ± 0.04 | 8 | (−0.7 ± 0.9) | | <5 |
| | 80 | 4 | 0.995 | 1.1 ± 0.2 | 18 | (1 ± 5) | | <40 |
| | 100 | 4 | 0.994 | 5.02 ± 1.12 | 22 | (2 ± 25) | | <30 |
| (2b) | 100 | 4 | 0.999 | 1.32 ± 0.14 | 11 | (−0.2 ± 1.3) | | <10 |
| (2c) | 100 | 4 | 0.9999 | 0.49 ± 0.01 | 2 | (−0.05 ± 0.24) | | <5 |
| (2d) | 100 | 3 | 0.9997 | 0.69 ± 0.08 | 11 | (0.6 ± 1.9) | | <30 |
| (2e) [e] | 100 | 4 | 0.9997 | 0.140 ± 0.007 | 5 | 2.58 ± 0.21 | 8 | 65 |
| (2f) [e] | 100 | 4 | 0.9999 | 0.098 ± 0.002 | 2 | 0.62 ± 0.04 | 6 | 39 |
| (2g) [e] | 100 | 4 | 0.999 | 0.106 ± 0.012 | 11 | 4.58 ± 0.35 | 8 | 81 |
| (2i) | 50 | 4 | 0.999 | 0.13 ± 0.01 | 8 | (0.5 ± 0.4) | 90 | <30 |
| | 60 | 4 | 0.999 | 0.29 ± 0.02 | 7 | 1.6 ± 0.5 | 31 | 36 |
| | 83 | 4 | 0.996 | 1.66 ± 0.29 | 17 | 22 ± 6 | 27 | 57 |
| | 100 | 4 | 0.9996 | 2.77 ± 0.03 | 1 | 112 ± 3 | 3 | 80 |
| (2j) | 60 | 4 | 0.997 | 0.286 ± 0.016 | 6 | 3.1 ± 0.3 | 10 | 52 |
| | 70 | 4 | 0.999 | 0.74 ± 0.05 | 7 | 15.6 ± 1.1 | 7 | 68 |
| | 81 | 4 | 0.990 | 3.23 ± 0.94 | 29 | 47 ± 20 | 42 | 59 |
| | 100 | 7 | 0.937 | 17 ± 6 | 34 | 330 ± 7 | 2 | 66 |
| (2m) | 100 | 4 | 0.999 | 47 ± 4 | 9 | (7.5 ± 8.2) | | <5 |
| (2n) [e] | 100 | 5 | 0.980 | 0.13 ± 0.03 | 27 | (−0.02 ± 0.94) | | <40 |

[a] Number of runs. [b] Correlation coefficient. [c] 90% confidence limits. [d] *i.e.* % reaction by $S_N1$ route at [piperidine] $10^{-1}$ mol l$^{-1}$. [e] Calculated from $k_{obs}$ values measured up to 30% conversion.

**Table 8.** First-order ($k_1$) and second-order ($k_2$) rate constants for the reactions of 14-substituted 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]-acridiniums with nucleophiles in chlorobenzene at 100 °C

| Compound | Nucleophile | $N$ [a] | $r$ [b] | Slope | | Intercept | $\frac{10^3k_1}{k_2 + 10k_1}$ [d] |
|---|---|---|---|---|---|---|---|
| | | | | $10^3k_2$/l mol$^{-1}$ s$^{-1}$ [c] | % Error | $10^5k_1$/s$^{-1}$ [c] | |
| (3a) | Piperidine | 5 | 0.994 | 24.9 ± 3.8 | 15 | (−4 ± 30) | <11 |
| (3b) | Piperidine | 4 | 0.9996 | 6.70 ± 0.38 | 6 | (5.6 ± 5.2) | <16 |
| (3c) | Piperidine | 3 | 0.9999 | 2.75 ± 0.05 | 2 | (−0.1 ± 0.6) | <2 |
| (3d) | Piperidine | 3 | 0.9999 | 2.41 ± 0.25 | 10 | (5.2 ± 6.6) | <30 |
| (3e) | Piperidine | 4 | 0.9999 | 1.99 ± 0.03 | 2 | (0.02 ± 0.52) | <3 |
| (3f) | Piperidine | 4 | 0.998 | 3.05 ± 0.26 | 9 | (−0.6 ± 1.3) | <2 |
| (3g) | Piperidine | 3 | 0.9999 | 2.51 ± 0.02 | 1 | (0.7 ± 0.8) | <6 |
| | Pyridine | 3 | 0.9991 | 0.013 ± 0.004 | 27 | (0.3 ± 0.3) | <80 |
| | Morpholine | 4 | 0.996 | 0.74 ± 0.14 | 19 | (8 ± 13) | <80 |
| (3m) | Piperidine | 5 | 0.998 | 56.2 ± 3.7 | 7 | (7 ± 11) | <3 |

[a] Number of runs. [b] Correlation coefficient. [c] 90% confidence limits. [d] Percentage reaction by $S_N1$ route at [Nucleophile] $10^{-1}$ mol l$^{-1}$.

The second-order rate constant for the reaction of benzyl chloride with piperidine at 80 °C in dimethylformamide is reported as 0.0555 l mol$^{-1}$ s$^{-1}$,[9] while those for the analogous reactions of the tri- and penta-cyclic derivatives (2o) and (3o) at 80 °C in chlorobenzene are respectively 0.0966 and 1.96 l mol$^{-1}$ s$^{-1}$.[3] The second-order rate constant for the reaction of the monocyclic derivative (1o) with piperidine at 100 °C in chlorobenzene was found to be twice that in dimethylformamide.[6] We conclude that in the reaction with piperidine at 80°, the tricyclic compound (2o) is a leaving group as good as chloride, while the pentacyclic (3o) is considerably better than chloride when attached to benzyl.

**Table 9.** Activation parameters [a]

| Compound | Reaction | $\Delta H^{\ddagger}_{373}$/kcal mol$^{-1}$ | $\Delta S^{\ddagger}_{373}$/cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| (2a) | $S_N2$ | 19.4 ± 2.1 | −17 ± 6 |
| (2i) | $S_N2$ | 14 ± 4 | −31 ± 13 |
| | $S_N1$ | 25.6 ± 0.8 | −4 ± 2 [b] |
| (2o) [c] | $S_N2$ | 15.8 ± 1.5 | −19 ± 5 |
| (3g) | $S_N2$ | 16.0 ± 0.3 | −28.2 ± 0.7 |
| (3o) [c] | $S_N2$ | 11.4 ± 2.2 | −25.4 ± 6.7 |

[a] Difficulties in the measurement of $k_{obs}$ at 100° (see Discussion section) prevented the calculation of meaningful values for (2j). [b] log $A$ equal to 12.4. [c] Data taken from ref. 3.

**Table 10.** First-order rate constants ($k_1$) for the reactions of *N*-alkyltetrahydrodibenzo[*c*,*h*]acridiniums with 2,4,6-triphenylpyridine in chlorobenzene at 120 °C

| Compound | 10$^3$[2,4,6-Triphenylpyridine]/mol l$^{-1}$ | $10^5k_1$/s$^{-1}$ | $10^5k_1$/s$^{-1}$ [a] |
|---|---|---|---|
| (3c) [b] | 55.4 | 1.89 | 1.97 ± 0.11 |
| | 0.00 | 2.05 | |
| (3g) [c] | 409 | 2.19 | |
| | 204 | 2.25 | 2.26 ± 0.05 |
| | 51.1 | 2.31 | |
| | 0.00 | 2.28 | |
| (3p) [d] | 24.5 | 0.790 | 0.81 ± 0.02 |
| | 0.00 | 0.824 | |

[a] Errors quoted are standard deviations. [b] Substrate concentration 2.10 × 10$^{-3}$ mol l$^{-1}$. [c] Substrate concentration 2.05 × 10$^{-3}$ mol l$^{-1}$. [d] Substrate concentration 1.00 × 10$^{-3}$ mol l$^{-1}$.

*Dependence of* $S_N2$ *Rates on Alkyl Group Structure.*—The second-order rate constants (Table 11) lead to several surprising conclusions. The tricyclic series (2) is the most complete and will be discussed first. The generally accepted [10,11] order for $S_N2$ rates is: benzyl > methyl > primary alkyl > secondary alkyl. By contrast we find: benzyl > methyl = secondary alkyl > primary alkyl. The conclusions reached from series (2) regarding the rate sequence are supported by the less complete data for series (1) and (3).

Quantitative values of relative rates, based on Et = 1 for various series are given in Table 14. Comparisons across Table 14 allow the following conclusions for reactivities of compounds in series (1)—(3) compared to their ethyl analogues. (a) The following react more slowly than typical: methyl in series (2) and (3), allyl in series (3). (b) The following react approximately at the same rate as expected: straight chain primary alkyl derivatives. (c) The following react faster than expected; benzyl in series (2) and (3), s-alkyl, and neopentyl.

The correlation with size is clear cut: groups larger than ethyl near the point of attachment tend to react faster than expected, those smaller than ethyl more slowly. Some support for this analysis is found from comparisons within the various series of alkyl derivatives given in Table 14. (a) Relative rates for methyl tend to increase: MeI < MeBr < MeCl. (b) Relative rates for n-alkyls show little variation. (c) Relative rates for s-alkyls show considerable variation in the sense RI > RBr > RCl. (d) Relative rates for neopentyl are only available for the bromide, but here the relative rate varies with the size (including expected solvation) of the nucleophile $EtO^- > Br^- > Cl^-$.

The steric substituent constants $E_s$ [12] were designed for the quantitative evaluation of steric effects. They have been very useful, as demonstrated by their recent use in correlating steric effects in the nucleophile with $S_N2$ rates.[13] However, no significant correlation was found between the logarithms of second-order rate constants for pyridiniums in series (1)—(3) and the Taft $E_s$ parameters.[12] This is not unexpected: whereas a single parameter could measure the *bulk* of substituents, it cannot measure the *shape* of the substituents, and changing shape with constant bulk may well affect different reactions in a different way.

McManus [14] has recently used differences between gas-phase proton affinities and $S_N2$ rates to calculate steric retardation factors (s.r.f.) for Me, Et, and Pr$^i$ as 2-substituents in pyridine. Few s.r.f. are available, but the relative rates for 2-H and 2-Me compounds in our reactions [1] indicate that

**Table 11.** Second-order rate constants ($k_2$) and relative reactivities for the reactions of *N*-substituted pyridinium cations in series (1)—(3) with piperidine in chlorobenzene at 100 °C

| | Series (1) | Series (2) | | Series (3) | | |
|---|---|---|---|---|---|---|
| *N*-Substituent | 10$^3k_2$/l mol$^{-1}$ s$^{-1}$ | 10$^3k_2$/l mol$^{-1}$ s$^{-1}$ | $k_2(2)/k_2(1)$ | 10$^3k_2$/l mol$^{-1}$ s$^{-1}$ | $k_2(3)/k_2(1)$ | $k_2(3)/k_2(2)$ |
| Benzyl | 4.94 [a] | 343 | 69 [b] | 4 446 | 900 [b,c] | 14 |
| Me | 0.600 | 5.02 | 8 | 24.9 | 42 | 5.0 |
| Et | 0.0306 | 1.32 | 43 | 6.70 | 219 | 5.1 |
| Pr$^n$ | | 0.49 | | 2.75 | | 5.6 |
| Bu$^n$ | | 0.69 | | 2.41 | | 3.5 |
| n-Pentyl | | 0.14 [d] | | 1.99 | | 14 |
| n-Hexyl | <0.008 | 0.098 [d] | >8 | 3.05 | >380 | 31 |
| n-Heptyl | | 0.106 [d] | | 2.51 | | 24 |
| Neopentyl | <0.008 | 0.13 [d] | >16 | | | |
| Pr$^i$ | 0.140 | 2.77 | 20 | | | |
| Bu$^s$ | 0.11 | 17 | 155 | | | |
| Allyl | 0.97 [e] | 47 | 48 | 56.2 | 58 | 1.2 |

[a] From ref. 6. [b] From ref. 3. [c] Extrapolated value. [d] Kinetics were followed up to 30% conversion only. [e] Kinetics were followed up to 45% conversion only.

**Table 12.** First-order rate constants and relative reactivities for the reactions of *N*-substituted pyridinium cations in series (1) and (2) with piperidine in chlorobenzene at 100 °C

| | Series (1) | Series (2) | |
|---|---|---|---|
| *N*-Substituent | $10^5k_1/s^{-1}$ | $10^5k_1/s^{-1}$ | $k_1(2)/k_1(1)$ |
| Pr$^i$ | 0.717 | 112 | 156 |
| Bu$^s$ | 3.2 | 330 | 103 |
| cyclopentyl | 25.4 | | |
| cyclohexyl | 3.10 | | |

**Table 13.** Observed ($k_{obs}$), first- ($k_1$), and second- ($k_2$) order rate constants for the reactions of pyridiniums (2o) and (3o) with thiourea in MeOH at 35 °C

Observed rate constants

| (2o) | | (3o) | |
|---|---|---|---|
| $10^5k_{obs}/s^{-1}$ | [Thiourea]/mol l$^{-1}$ | $10^5k_{obs}/s^{-1}$ | [Thiourea]/mol l$^{-1}$ |
| 0.210 | 0.08 [a] | 0.591 | 0.001 28 [a] |
| 0.358 | 0.12 [a] | 2.42 | 0.032 [a] |
| 0.415 | 0.16 [a] | 6.76 | 0.06 [b] |
| 0.597 | 0.24 [b] | 8.86 | 0.08 [a] |
| | | 15.2 | 0.16 [b] |

First- and second-order rate constants

| Compound | $r$ [c] | $N$ [d] | $10^4k_2$/ [e] l mol$^{-1}$ s$^{-1}$ | $10^6k_1$/ [c] s$^{-1}$ | $k_2/k_2$ (2o) |
|---|---|---|---|---|---|
| $PhCH_2Br$ | | | 141 [f] | | 613 |
| (3o) | 0.991 | 5 | 9.50 ± 0.14 | (4 ± 15) [g] | 41 |
| (2o) | 0.989 | 4 | 0.23 ± 0.07 | (0.5 ± 1.1) [g] | 1 |

[a] Concentration of substrate $3.2 \times 10^{-5}$ mol l$^{-1}$. [b] Concentration of substrate $1.6 \times 10^{-3}$ mol l$^{-1}$. [c] Correlation coefficient. [d] Number of runs. [e] 90% Confidence limit. [f] R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Am. Chem. Soc.*, 1952, **74**, 5130. [g] Not significantly different from zero.

attempted correlations of our rates with s.r.f. will not succeed.

*Relative* $S_N1$ *Rates.*—The higher reactivity (by a factor of eight) of the cyclopentyl compared with the cyclohexyl derivative (Table 12) accords with the factor of 16 reported for the hydrolysis of the corresponding tosylates [15] at 60° and the factor of 120 for hydrolysis of 1-chloro-1-methylcycloalkanes [16] at 25°.

Available quantitative comparisons for isopropyl and s-butyl compounds are given in Table 15. The somewhat higher rates found for s-butyl relative to the isopropyl derivative agree with those for the hydrolysis of bromides.

*Activation Parameters.*—From the values of rate constants at several temperatures in Table 7, activation parameters were calculated (Table 9) for the tricyclic derivatives (2a, i, j) and the pentacyclic compound (3g).

We have previously reported activated parameters for the $S_N1$ and $S_N2$ components of the reactions of 1-(*p*-methoxybenzyl)- and 1-(2-furfuryl)-2,4,6-triphenylpyridinium with piperidine in chlorobenzene [8] and for the corresponding $S_N2$ reaction of a variety of *N*-benzylpyridiniums.[3] As previously pointed out,[3] these results provide strong support for the assignment of reaction mechanism: the parameters found for $S_N1$ ($\Delta H^{\ddagger}$ 26 kcal mol$^{-1}$; $\Delta S^{\ddagger}$ −4 cal mol$^{-1}$ K$^{-1}$) and for $S_N2$ ($\Delta H^{\ddagger}$ 11—20 kcal mol$^{-1}$; $\Delta S^{\ddagger}$ −30 to −17 cal mol$^{-1}$ K$^{-1}$) are typical for those previously reported for these types of reaction. The new data given in Table 9 are entirely in line with the previous treatment, supporting the separation of the $S_N1$ and $S_N2$ components and the assignment of the reaction mechanisms.

## Experimental

*Compounds.*—The following were prepared by others and their preparation has been, or will be, reported elsewhere: (i) 2,4,6-triphenylpyridiniums: 1-(s-butyl) (1j) as $BF_4^-$, m.p. 165—167 °C; [17] 1-(cyclopentyl) (1h) as $BF_4^-$, m.p. 163—164

**Table 14.** Second-order relative rates for the reaction of *N*-alkyl- and *N*-benzyl-pyridiniums (1)—(3) with piperidine in chlorobenzene at 100 °C and for the reaction of benzyl and alkyl halides with nucleophiles

| | | | | Reactions | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Substituent | Series (1) + piperidine | Series (2) + piperidine | Series (3) + piperidine | RI + $PhO^-$ [a] | RBr + $EtO^-$ [b] | RI + $NEt_3$ [c] | RBr + $Cl^-$ [d] | RBr + $Br^-$ * [e] | RCl + KI [f] | RLG + Nu [g] |
| Benzyl | 161 | 245 | 664 | | | | | | 80 | 120 |
| Allyl | 32 [h] | 35 | 8.4 | | | | | | 32 | 40 |
| Me | 20 | 3.8 | 3.7 | 4.5 | 18 | 11 | 3.7 | 76 | 80 | 30 |
| Et | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Pr$^n$ | | 0.37 | 0.41 | 0.39 | 0.31 | 0.19 | 0.69 | 0.65 | 0.43 | 0.4 |
| Bu$^n$ | | 0.50 | 0.36 | 0.36 | 0.23 | 0.14 | | | 0.40 | 0.4 |
| n-Pentyl | | 0.11 [i] | 0.30 | 0.16 | 0.20 | | | | 0.53 | |
| n-Hexyl | <0.3 | 0.07 [i] | 0.5 | 0.34 | | | | | 0.52 | |
| n-Heptyl | | 0.08 [i] | 0.37 | 0.33 | | 0.10 | | | 0.50 | |
| Neopentyl | <0.3 | 0.10 [i] | | | 0.0042 | | $6 \times 10^{-6}$ | $1 \times 10^{-5}$ | | $1 \times 10^{-5}$ |
| Pr$^i$ | 4.6 | 2.1 | | 0.34 | | 0.02 | 0.02 | 0.01 | 0.008 | 0.025 |
| Bu$^s$ | 3.6 | 13 | | 0.38 | | | | | 0.008 | 0.03 |

[a] In dry EtOH at 42.5 °C; from: D. Segaller, *J. Chem. Soc.*, 1913, **103**, 1154; 1914, **105**, 106. [b] In dry EtOH at 55 °C; from: ref. 10, p. 432; I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 1946, 157; M. L. Dhar, E. D. Hughes, C. K. Ingold, and S. Masterman, *ibid.*, 1948, 2055. [c] In acetone at 100 °C, from ref. 10, p. 435; N. Menschutkin, *Z. Phys. Chem.*, 1890, **5**, 589. [d] In dimethylformamide at 25 °C, from: S. Hartshorn, 'Aliphatic Nucleophilic Substitution'; Cambridge University Press; Cambridge, 1973, p. 32. [e] In acetone at 25 °C, from: ref. 10, p. 436; P. B. D. de la Mare, *J. Chem. Soc.*, 1955, 3180. [f] In acetone at 50 °C, from: J. Hine, 'Physical Organic Chemistry,' McGraw Hill, New York, 1962, 2nd. edn., p. 176; J. B. Conant and R. E. Hussey, *J. Am. Chem. Soc.*, 1925, **47**, 476; J. B. Conant, W. R. Kirner, and R. E. Hussey, *ibid.*, 1925, **47**, 488. [g] Average relative rates of alkyl systems from ref. 11. [h] Kinetics were followed up to 45% conversion. [i] Kinetics were followed up to 30% conversion.

**Table 15.** First-order relative rates for the reactions of *N*-isopropyl- and *N*-s-butyl-pyridiniums (1) and (2) with piperidine in chlorobenzene and for the solvolysis of bromides at 100 °C

| *N*-Substituent or R | Series (1) + piperidine | Series (2) + piperidine | RBr + $H_2O$ [a] |
|---|---|---|---|
| $Pr^i$ | 1.0 | 1.0 | 1.0 |
| $Bu^s$ | 4.5 | 2.9 | 2.1 |

[a] In $HCO_2H$; from L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 1940, 945.

**Table 16.** Kinetic wavelengths (nm) for compounds in series (1)—(3) and extinction coefficients of 2,4,6-triphenylpyridine (4)

| Compound designation | Series (1) Kinetic λ | Series (1) $\varepsilon_4$ [a] | Series (2) Kinetic λ | Series (3) Kinetic λ |
|---|---|---|---|---|
| a | 307 | 7 700 | 355 | 360 |
| b | 307 | 7 700 | 360 | 360 |
| c | | | 355 | 360 |
| d | | | 355 | 360 |
| e | | | 350 | 360 |
| f | 307 | 7 700 | 350 | 360 |
| g | | | 350 | 385 |
| i | 306 | 7 500 | 347 | |
| j | 312 | 8 000 | 348 | |
| k | 310 | 8 000 | | |
| l | 309 | 7 900 | | |
| m | 309 | 7 900 | 360 | 360 |
| n | 318 | 7 650 | 360 | |
| o | | | 360 | 400 |
| p | | | | 392 |

[a] In 2% (v/v) chlorobenzene in ethanol.

°C; [17] 1-neopentyl (1n) as $BF_4^-$, m.p. 244—245 °C; [17] (ii) 2,4-diphenyl-5,6-dihydrobenzo[*h*]quinoliniums: 1-n-butyl (2d) as $BF_4^-$, m.p. 97—98 °C; [18] 1-isopropyl (2i) as $ClO_4^-$, m.p. 140—142 °C; [17] 1-s-butyl (2j) as $ClO_4^-$, m.p. 137—139 °C; [17] 1-s-butyl (2j) as $BF_4^-$, m.p. 130—132 °C; [19] 1-benzyl (2o) as $ClO_4^-$, m.p. 152 °C; [18] (iii) 7-phenyl-5,6,8,9-tetrahydrodibenzo[*a*,*h*]acridiniums: 14-methyl (3a) as $CF_3SO_3^-$, m.p. 264 °C; [20] 14-ethyl (3b) as $ClO_4^-$, m.p. 257—258 °C; [21] 14-n-butyl (3d) as $CF_3SO_3^-$, m.p. 192—193 °C; [22] 14-n-hexyl (3f) as $CF_3SO_3^-$, m.p. 158—159 °C [23] (previously reported [20] as m.p. 101—102 °C, probably a polymorphic form); 14-n-heptyl (3g) as $CF_3SO_3^-$, m.p. 183 °C; [22] 14-allyl (3m) as $CF_3SO_3^-$, m.p. 127—129 °C; [17] 14-benzyl (3o) as $CF_3SO_3^-$, m.p. 170—171 °C; [20] 14-phenylethyl (3p) as $CF_3SO_3^-$, m.p. 229—231 °C.[20]

*Preparation of pyridinium salts.* The pyrylium (0.01 mol) suspended in absolute ethanol (20 ml) was treated with the appropriate amine (0.02 mol) dropwise at 20 °C over 10 min. After stirring for 10 h, ether (100 ml) was added, and the precipitate collected (see Table 1).

*Kinetic Measurements.*—The kinetics were followed by u.v. spectrophotometry under pseudo-first-order conditions following the procedure already described.[6] The concentrations of pyridinium ranged from $3.2 \times 10^{-5}$ to $1.6 \times 10^{-3}$ mol $l^{-1}$ and those of nucleophile from 0.004 to 1.28 mol $l^{-1}$. Pseudo-first-order rate constants for series (1) were calculated from the plot of $\ln(a/a - x) = \ln(\varepsilon_1 - \varepsilon_4)/(\varepsilon - \varepsilon_4)$ *versus* time, while those of series (2) and (3) from the plot of $\ln(D_0/D)$ *versus* time, the absorbance of the corresponding pyridines (5) and (6) being zero at the kinetic wavelength. Second-order rate constants, unless otherwise stated, were calculated from the slope of the plot of $k_{obs}$ *versus* piperidine concentration. For definition and calculation of errors, and for estimate of the precision of $k_{obs}$, see ref. 1. The extinction coefficients for (4) and the kinetic wavelength are recorded in Table 16.

The u.v. spectrum (EtOH) of pyridine (5) shows a maximum at 322 nm (12 950) while that of pyridine (6) has maxima at 335 (15 950) and 282 nm (12 730) and an inflection at 292 nm (10 550).

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## References

1 Part 8, A. R. Katritzky, Y. X. Ou, J. Ellison, and G. Musumarra, preceding paper.
2 For preliminary communications of part of this work see (*a*) A. R. Katritzky, G. Musumarra, K. Sakizadeh, S. M. M. El-Shafie, and B. Jovanovic, *Tetrahedron Lett.*, 1980, 2697; (*b*) A. R. Katritzky, G. Musumarra, and K. Sakizadeh, *ibid.*, p. 2701.
3 A. R. Katritzky, A. M. El-Mowafy, G. Musumarra, K. Sakizadeh, C. Sana-Ullah, S. M. M. El-Shafie, and S. S. Thind, *J. Org. Chem.*, 1981, **46**, 3823.
4 A. R. Katritzky, J. Adamson, E. M. Elisseou, G. Musumarra, R. C. Patel, K. Sakizadeh, and W. K. Yeung, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1041.
5 A. R. Katritzky, *Tetrahedron*, 1980, **36**, 679.
6 A. R. Katritzky, G. Musumarra, K. Sakizadeh, and M. Misic-Vukovic, *J. Org. Chem.*, 1981, **46**, 3820.
7 A. R. Katritzky and J. M. Lloyd, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2347.
8 A. R. Katritzky, G. Musumarra, and K. Sakizadeh, *J. Org. Chem.*, 1981, **46**, 3831.
9 F. Jamamoto, H. Morita, and S. Oae, *Heterocycles*, 1975, **3**, 1.
10 C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, 2nd. edn., p. 555.
11 A. Streitwieser, ' Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, p. 13.
12 R. W. Taft, Jr., ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 598.
13 D. F. De Tar, *J. Org. Chem.*, 1980, **45**, 5174.
14 S. P. McManus, *J. Org. Chem.*, 1981, **46**, 635.
15 J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 1951, **73**, 5034.
16 H. C. Brown, R. S. Fletcher, and R. B. Joahnnsen, *J. Am. Chem. Soc.*, 1951, **73**, 212.
17 A. R. Katritzky, J. M. Lloyd, and R. C. Patel, *J. Chem. Soc., Perkin Trans. 1*, 1982, 117.
18 A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1895.
19 A. R. Katritzky, J. Marquet, J. M. Lloyd, and J. G. Keay, following paper.
20 A. R. Katritzky, A. M. El-Mowafy, L. Marzorati, R. C. Patel, and S. S. Thind, *J. Chem. Res.* (*S*), 1980, 310; (*M*) 1980, 4001.
21 S. S. Thind, Ph.D. Thesis, University of East Anglia, 1979.
22 A. R. Katritzky and A. M. El-Mowafy, *J. Org. Chem.*, 1982, **47**, 3506.

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