# Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 6.[1] Reactions of *N*-(Substituted Benzyl)-azaheterocyclonium Compounds with Piperidine

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The preparation is described of series of *N*-(*p*-substituted)benzyl and *N*-(2-furfuryl) compounds with different heterocyclic leaving groups. First- and second-order rate constants for their reactions with piperidine in chlorobenzene are measured and discussed. Plots of $k_2$ values for substituted compounds *versus* $k_2$ for the parent *N*-benzyl derivative are linear for each substituent despite variable temperature of measurement.

We previously reported (a) the effect of substituents in the *N*-benzyl group on the mechanism and rate of the reaction of 1-benzyl-2,4,6-triphenylpyridinium with piperidine[2] and (b) the effect of changing the leaving group on this reaction.[3] The results were sufficiently interesting to warrant investigation of the simultaneous change of both benzyl substitution and leaving group: we now report on this subject.

*Preparation of Substrates.*—Pyryliums (1a)—(11a) were prepared by literature procedures or by modifications of them (see Experimental section) and condensed with the relevant benzylamines and 2-furfurylamine to give the azonium derivatives listed in Table 1.

In many cases the reaction was performed by the standard procedure in dichloromethane at 20 °C (method A); for the more hindered pyryliums it was advantageous to add a little acetic acid[4] (method B). Difficulties were encountered in the preparation of some of the *p*-methoxy derivatives: (13d) was obtained successfully in ether, but for the tricyclic (19d) it was necessary to work at $-15$ °C to avoid decomposition of this very reactive pyridinium. Reactions of *p*-methoxybenzylamine with the α-t-butylpyryliums (3a) and (6a) and with the pentacyclic pyrylium (11a) gave only the corresponding pyridines [(3b), (6b), and (11b), respectively]: presumably in each case the intermediate *N*-*p*-methoxybenzyl cation had undergone rapid solvolysis.

Pyridines (1b)—(11b) required as reference samples in the kinetic work were obtained from the pyrylium by reaction with ammonia, or some times with *p*-methoxybenzylamine.

*Kinetic Measurements.*—Reactions with piperidine as nucleophile in chlorobenzene solvent were followed spectrophotometrically under pseudo-first-order conditions as previously described.[5] In most cases the observed pseudo-first-order rate constants (Table 2) were linear with [piperidine]. However, difficulties were encountered with pyridiniums containing fused indene systems and no useful results could be obtained with compounds (20a) or (18d) (100 °C); the formation of green colours suggested deprotonation at the $CH_2$ group of the fused five-membered ring with the formation of an anhydro-base, and satisfactory first-order plots were not obtained.

For systems (16) and (21), curves were obtained for (16a) and (21d) for plots of $\ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ against time. We believe that this is also due to slow deprotonation to the anhydro-base (23). For the more reactive (16d) and (16e) individual kinetic runs were quite acceptable. However, the plots of $k_{\text{obs.}}$ *versus* [piperidine] gave slightly negative slopes. We believe that the values of $k_1$ calculated from the plots are valid, but that $k_2$ cannot be found as it is less than the deprotonation rates to yield derivatives of type (23). Colour formation during the runs supports this interpretation. Compound (19d) could not be measured because it was too reactive. Compound (15) derived from pyrylium (4a) could not be measured because the u.v. spectra of pyridiniums and pyridines were too close.

As before,[6] the observed rate variations can be interpreted in terms of $S_N1$ and/or $S_N2$ mechanisms: calculated $S_N1$ and $S_N2$ rate constants are collected in Table 3.

*Second-order Kinetic Rates for* N-*Benzyl and* N-(*Substituted Benzyl*) *Compounds.*—Most of the *N*-benzyl derivatives have been measured previously[7] and the present rates are in agreement within the experimental error.

For reaction of (22c) with piperidine, the temperature dependence is measured and given in Table 4. The Arrhenius parameters * ($\Delta H_{373}$ 12.0 ± 3.7 kcal mol$^{-1}$ and $\Delta S$ $-26.7$ ± 12.1 cal mol$^{-1}$ K$^{-1}$) for this compound match with those obtained for (22a).[7]

Attempted Hammett treatment of the present data for the *N*-(substituted benzyl) compounds is difficult because of (a) the few compounds in each series, (b) curvature, and (c) uncertainty as to which Hammett constants should be used.

However, plots of log $k_2$ for substituted benzyl derivatives against log $k_2$ for the parent benzyl derivatives (Figure 1) for the series (12) (at 40, 60, and 100 °C), (13), (14), (17), and (22), show linearity for each substituent, despite the different temperatures used. The correlations have slopes close to unity (Table 5). These

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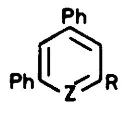
* The error is given at the 90% confidence limit.

TABLE 1

Preparation of pyridinium tetrafluoroborates from pyryliums

| Compd. | Pyridinium ring substituents | *N*-Substituent | Method | Recryst. solvent [a] | M.p. (°C) | Yield (%) | Found (%) | | | Formula | Required (%) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H | N | | C | H | N |
| (13a) | 2-Methyl-4,6-diphenyl | $PhCH_2$ | A | EtOH [b] | 257—258 [c] | 86 | 70.9 | 5.4 | 3.1 | $C_{25}H_{22}BF_4N$ | 70.9 | 5.2 | 3.3 |
| (13b) | | $MeC_6H_4CH_2(p)$ | A | EtOH | 220—221 [d] | 45 | 71.2 | 5.6 | 3.2 | $C_{26}H_{24}BF_4N$ | 71.4 | 5.5 | 3.2 |
| (13c) | | $ClC_6H_4CH_2(p)$ | A | EtOH | 229—230 | 75 | 65.2 | 4.7 | 2.9 | $C_{25}H_{21}BClF_4N$ | 65.6 | 4.6 | 3.1 |
| (13d) | | $MeOC_6H_4CH_2(p)$ | C | $Me_2CO–Et_2O$ | 161—162 | 60 | 68.5 | 5.2 | 3.1 | $C_{26}H_{24}BF_4NO$ | 68.9 | 5.3 | 3.1 |
| (13e) | | 2-Furfuryl | A | $Me_2CO–Et_2O$ | 160—161 | 75 | 66.5 | 4.9 | 3.4 | $C_{23}H_{20}BF_4NO$ | 66.8 | 4.9 | 3.4 |
| (14a) | 2-t-Butyl-4,6-diphenyl | $PhCH_2$ | B | EtOH | 155—156 [e] | 60 | | | | $C_{28}H_{28}BF_4N$ | | | |
| (14b) | | $MeC_6H_4CH_2(p)$ | A | EtOH [b] | 139—140 | 77 | 72.7 | 6.4 | 2.8 | $C_{29}H_{30}BF_4N$ | 72.7 | 6.3 | 2.9 |
| (14c) | | $ClC_6H_4CH_2(p)$ | A | EtOH | 169—170 [f] | 81 | 67.4 | 5.3 | 2.7 | $C_{28}H_{27}BClF_4N$ | 67.2 | 5.4 | 2.8 |
| (16a) | 2-t-Butyl-5*H*-4-phenylindeno-[1,2-*b*]pyridinium | $PhCH_2$ | A | EtOH | 187—188 | 69 | 73.0 | 6.1 | 2.9 | $C_{29}H_{28}BF_4N$ | 73.0 | 5.9 | 2.9 |
| (16b) | | $MeC_6H_4CH_2(p)$ | A | EtOH | 167—168 | 60 | 73.2 | 6.3 | 2.8 | $C_{30}H_{30}BF_4N$ | 73.3 | 6.2 | 2.9 |
| (16c) | | $ClC_6H_4CH_2(p)$ | A | $EtOH–Me_2CO$ | 230—231 | 56 | 68.2 | 5.4 | 2.7 | $C_{29}H_{27}BClF_4N$ | 68.1 | 5.3 | 2.7 |
| (16d) | | $MeOC_6H_4CH_2(p)$ | A | $Me_2CO–Et_2O$ [b] | 139—140 (decomp.) | 75 | 70.8 | 5.9 | 2.7 | $C_{30}H_{30}BF_4NO$ | 71.0 | 6.0 | 2.8 |
| (16e) | | 2-Furfuryl | A | EtOH | 182—183 | 66 | 69.2 | 5.4 | 2.9 | $C_{27}H_{26}BF_4NO$ | 69.4 | 5.6 | 3.0 |
| (17a) | 2-t-Butyl-5,6-dihydro-4-phenylbenzo[*h*]quinolinium | $PhCH_2$ | B | $Me_2CO–Et_2O$ | 136—137 [g] | 57 | | | | $C_{30}H_{30}BF_4N$ | | | |
| (17b) | | $MeC_6H_4CH_2(p)$ | B | $Me_2CO–Et_2O$ | 113—114 | 56 | 73.4 | 6.4 | 2.7 | $C_{31}H_{32}BF_4N$ | 73.7 | 6.4 | 2.8 |
| (17c) | | $ClC_6H_4CH_2(p)$ | B | $Me_2CO–Et_2O$ | 137—138 | 62 | 68.7 | 5.5 | 2.6 | $C_{30}H_{29}BClF_4N$ | 68.5 | 5.6 | 2.7 |
| (18a) | 5*H*-2,4-Diphenylindeno-[1,2-*b*]pyridinium | $PhCH_2$ | A | EtOH | 211—212 [h] | 68 | 74.9 | 4.7 | 2.8 | $C_{31}H_{24}BF_4N$ | 74.9 | 4.9 | 2.8 |
| (18d) | | $MeOC_6H_4CH_2(p)$ | A | $Me_2CO–Et_2O$ | 133—134 | 61 | 72.6 | 4.8 | 2.7 | $C_{32}H_{26}BF_4NO$ | 72.9 | 5.0 | 2.7 |
| (19d) | 5,6-Dihydro-2,4-diphenylbenzo[*h*]quinolinium | $MeOC_6H_4CH_2(p)$ | D | *i* | 78—79 | 67 | 73.0 | 5.1 | 2.5 | $C_{33}H_{28}BF_4NO$ | 73.2 | 5.2 | 2.6 |
| (20a) | 4-Phenylbisindeno[1,2-*b*]-pyridinium | $PhCH_2$ | A | $Me_2CO–Et_2O$ | 220—221 | 52 | 75.3 | 4.8 | 2.6 | $C_{32}H_{24}BF_4N$ | 75.5 | 4.8 | 2.8 |
| (20d) | | $MeOC_6H_4CH_2(p)$ | B | *i* | 170 [j] | 70 | 73.2 | 4.8 | 2.4 | $C_{33}H_{26}BF_4NO$ | 73.5 | 4.9 | 2.6 |
| (21a) | 5,6-Dihydro-4-phenylindeno[1,2-*b*]-benzo[*h*]quinolinium | $PhCH_2$ | A | $Me_2CO–Et_2O$ | 172—173 [k] | 65 | 75.8 | 5.1 | 2.7 | $C_{33}H_{26}BF_4N$ | 75.7 | 5.0 | 2.7 |
| (21d) | | $MeOC_6H_4CH_2(p)$ | B | *i* | 109—110 | 72 | 73.4 | 5.0 | 2.4 | $C_{34}H_{28}BF_4NO$ | 73.8 | 5.1 | 2.5 |
| (22a) | 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium | $PhCH_2$ | B | $Me_2CO–Et_2O$ | 159—160 | 57 | 75.8 | 5.4 | 2.8 | $C_{34}H_{28}BF_4N$ | 76.0 | 5.3 | 2.6 |
| (22b) | | $MeC_6H_4CH_2(p)$ | B | $Me_2CO–Et_2O$ | 161—162 | 70 | 76.0 | 5.6 | 2.5 | $C_{35}H_{30}BF_4N$ | 76.2 | 5.5 | 2.5 |
| (22c) | | $ClC_6H_4CH_2(p)$ | B | $Me_2CO–Et_2O$ | 162—163 | 60 | 71.8 | 4.9 | 2.7 | $C_{34}H_{27}BClF_4N$ | 71.4 | 4.8 | 2.5 |

[a] Prisms unless otherwise indicated. [b] Plates. [c] Lit. m.p. 227—229 °C (A. R. Katritzky, R. C. Patel, and M. Shanta, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1888). [d] Lit. m.p. 232—235 °C (footnote *c*). [e] Lit. m.p. 151 °C.[9] [f] Lit. m.p. 155—157 °C.[9] [g] Lit. m.p. 130—132 °C.[4b] [h] Lit. m.p. 226 °C.[7] [i] The compound decomposes upon attempted recrystallisation. [j] With sublimation. [k] Lit. m.p. 120 °C.[7]



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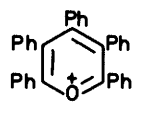
(3) R = $Bu^t$



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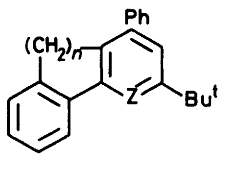

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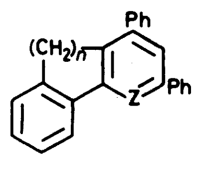
(6) $n$ = 2



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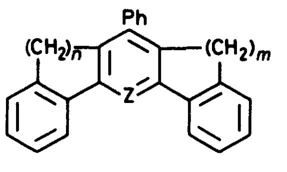
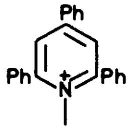


(9) $n = m = 1$
(10) $n = 1$, $m = 2$
(11) $n = m = 2$

a; $Z = O^+$ b; Z = N



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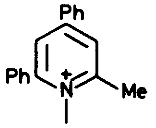

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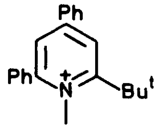

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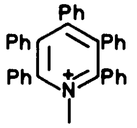

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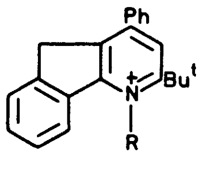

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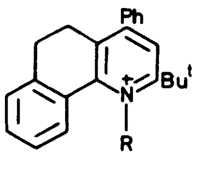

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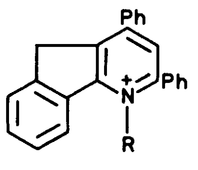

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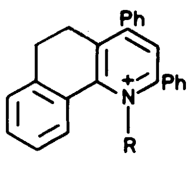

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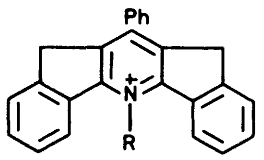

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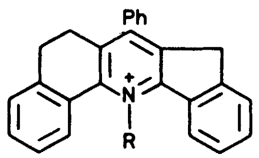

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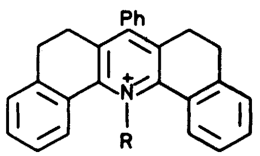


(22)

a; R = $PhCH_2$ b; R = $p$-$MeC_6H_4CH_2$ c; R = $p$-$ClC_6H_4CH_2$ d; R = $p$-$MeOC_6H_4CH_2$ e; R = 2-furyl-$CH_2$

plots are considerably superior to those where the log $k_2$ for the other series are plotted against the log $k_2$ for reference series (12) (Figure 2).

Although standard l.f.e.r. treatments of second-order rates are not possible due to the above-mentioned reasons, empirical correlations such as those reported in Figure 1 and Table 5 demonstrate the consistency of the present set of data and represent a useful tool for the prediction of reactivities in these reactions.

*First-order Kinetic Rates.*—Within each series the first-order rates increase in the order $p$-Cl < H < $p$-Me ⩽ $p$-OMe or 2-furfuryl. For the monocyclic series (13) and (14), a significant $S_N1$ component is detected for the $N$-($p$-methoxybenzyl) (d) and $N$-(2-furfuryl) (e) derivatives, as already observed for the parent series (12).[6] We have previously shown [7] that significant first-order rates can also occur for unsubstituted $N$-benzyl compounds, if the leaving group structure is changed [*e.g.* series (14) and (17)]. This finding is now confirmed for $p$-methyl- and $p$-chloro-substituted benzyls such as (14b), (17b) and (17c). No significant $S_N1$ component was found for (22b and c), in accord with what was found for (22a).[7]

*Conclusions.*—All the compounds studied react by the $S_N2$ mechanism. Second-order rates for substituted benzyl derivatives are found to be linearly correlated

TABLE 2

Pseudo-first-order rate constants ($k_{obs.}$) for the reactions of *N*-substituted-benzyl- and *N*-furfuryl-azaheterocycloniums with piperidine in chlorobenzene

| | $10^5k_{obs.}/s^{-1}$ | | | |
|---|---|---|---|---|
| [Piperidine]/M | (13b) [a] (100 °C) | (13c) [a] (100 °C) | (13d) [a] (100 °C) | (13e) [a] (100 °C) |
| 0.04 | | | 24.9 | 21.8 |
| 0.08 | 1.59 | | 27.1 | 27.2 |
| 0.12 | 2.21 | 2.03 | 29.6 | 32.3 |
| 0.16 | 3.13 | 2.78 | 30.8 | 35.5 |
| 0.20 | | 3.56 | | |
| 0.24 | 4.60 | | | |

| | $10^5k/s^{-1}$ | |
|---|---|---|
| [Piperidine]/M | (14b) (100 °C) | (14c) [a] (100 °C) |
| 0.0008 | 124 [b] | |
| 0.04 | 147 [a] | 8.70 |
| 0.08 | 170 [a] | 15.9 |
| 0.12 | 196 [a] | 23.2 |
| 0.16 | | 28.7 |

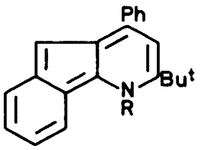
| | (16d) [b] (60 °C) |
|---|---|
| [Piperidine]/M | $10^5k_{obs.}/s^{-1}$ |
| 0.000 96 | 31.4 |
| 0.001 90 | 28.5 |
| 0.0026 | 28.8 |

| | $10^5k_{obs.}/s^{-1}$ | |
|---|---|---|
| [Piperidine]/M | (16e) [b] (60 °C) | (18d) [b] (60 °C) |
| 0.000 32 | | |
| 0.000 64 | 137 | |
| 0.000 80 | 141 | 6.9 |
| 0,0016 | 123 | 6.9 |
| 0.0024 | 120 | 7.1 |
| 0.0032 | | 7.3 |

| | $10^5k_{obs.}/s^{-1}$ | | |
|---|---|---|---|
| [Piperidine]/M | (17b) [b] (60 °C) | (17c) [b] (60 °C) | (22b) [b] (30 °C) |
| 0.0016 | 310 | 9.51 | |
| 0.0032 | 319 | | 45.6 |
| 0.0064 | 348 | 23.4 | 90.4 |
| 0.0096 | | | 131 |
| 0.013 | 395 | 43.9 | |
| 0.016 | | 51.3 | 217 |

[a] Concentration of pyridinium $1.6 \times 10^{-3}$M. [b] Concentration of pyridinium $3.2 \times 10^{-5}$M.

with those of the parent benzyl derivatives (*cf.* Table 5 and Figure 1), with slopes close to unity, showing the constancy of substituent effects in the examined compounds. A significant $S_N1$ component can be detected if the N-substituent or the leaving group are changed, supporting, in our opinion, previous evidence for the occurrence of simultaneous $S_N2$–$S_N1$ mechanisms.[2,3,6,7]



(23)

This work confirms and extends the conclusion reported in Parts 2 and 3.

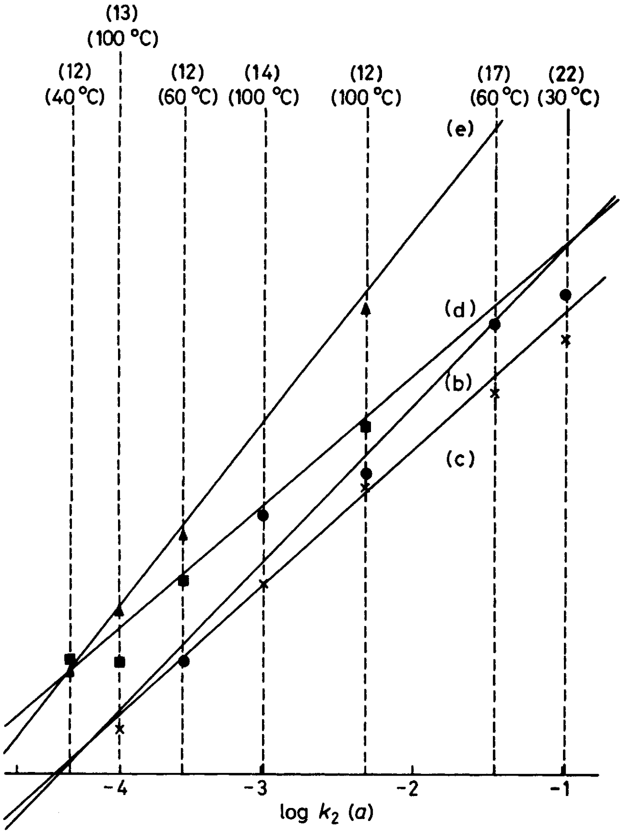


FIGURE 1 Plot of the logarithms of second-order rate constants (log $k_2$) for the reactions of *N*-(*p*-methylbenzyl)- (b), *N*-(*p*-chlorobenzyl)- (c), *N*-(*p*-methoxybenzyl)- (d), and *N*-(2-furfuryl)- (e) pyridiniums *versus* log $k_2$ for the corresponding *N*-benzyl compounds (a)

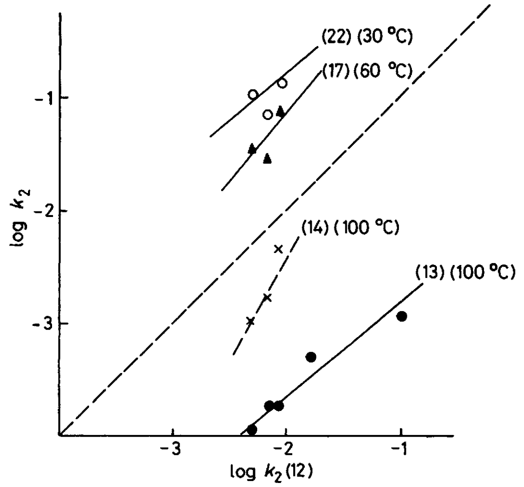


FIGURE 2 Plot of the logarithms of second-order rate constants (log $k_2$) for the reactions of *N*-(substituted benzyl)- and *N*-(2-furfuryl)-pyridiniums (13) at 100 °C, (14) at 100 °C, (17) at 60 °C, and (22) at 30 °C with piperidine in chlorobenzene *versus* log $k_2$ for *N*-(substituted benzyl)-2,4,6-triphenylpyridinium (12) at 100 °C

TABLE 3

First- and second-order rate constants for the reactions of *N*-substituted-benzyl- and *N*-furfuryl-azaheterocycloniums with piperidine in chlorobenzene

| | | | | Slope | | Intercept | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $T$ (°C) | $N$ [a] | $r$ [b] | $10^3k_2$ [c]/l mol$^{-1}$ s$^{-1}$ | Error (%) | $10^5k_1$ [c,d]/s$^{-1}$ | Error (%) | $\frac{10^3\,k_1}{k_2 + 10\,k_1}$ [e] |
| (13a) [f] | 100 | 5 | 0.997 | $0.119 \pm 0.013$ | 11 | $<1$ $(0.30 \pm 0.30)$ | | $<33$ |
| (13b) | 100 | 4 | 0.998 | $0.191 \pm 0.022$ | 11 | $<0.4$ $(0.02 \pm 0.35)$ | | $<16$ |
| (13c) | 100 | 3 | 0.999 | $0.191 \pm 0.013$ | 7 | $(-0.27 \pm 0.22)$ | | |
| (13d) | 100 | 4 | 0.991 | $0.51 \pm 0.14$ | 28 | $23.1 \pm 1.5$ | 6 | 82 |
| (13e) | 100 | 4 | 0.994 | $1.16 \pm 0.27$ | 23 | $17.7 \pm 2.9$ | 16 | 60 |
| (14a) [f] | 100 | 5 | 0.998 | $1.07 \pm 0.08$ | 7 | $8.0 \pm 2.2$ | 27 | 43 |
| (14b) | 100 | 4 | 0.9996 | $6.01 \pm 0.34$ | 6 | $123 \pm 3$ | 2 | 67 |
| (14c) | 100 | 4 | 0.998 | $1.68 \pm 0.22$ | 13 | $<5$ $(2.3 \pm 2.4)$ | | $<22$ |
| (16d) | 60 | 3 | 0.876 | $(-17 \pm 60)$ | | $33 \pm 12$ | 35 | |
| (16e) | 60 | 4 | 0.929 | $(-118 \pm 97)$ | | $146 \pm 15$ | 10 | |
| (17a) [f] | 60 | 8 | 0.999 | $36.3 \pm 1.0$ | 3 | $6.2 \pm 3.8$ | 61 | 2 |
| (17b) | 60 | 4 | 0.999 | $75.8 \pm 8.3$ | 11 | $297 \pm 6$ | 2 | 28 |
| (17c) | 60 | 4 | 0.999 | $29.4 \pm 1.9$ | 6 | $4.8 \pm 2.0$ | 41 | 2 |
| (18a) [f] | 100 | 4 | 0.995 | $106 \pm 14$ | 13 | $11.2 \pm 0.7$ | 7 | 1 |
| (18d) | 60 | 4 | 0.944 | $1.7 \pm 1.3$ | 72 | $6.70 \pm 0.27$ | 4 | 28 |
| (22a) [f] | 30 | 6 | 0.999 | $105 \pm 4$ | 4 | $<1$ $(0.4 \pm 0.8)$ | | $<0.1$ |
| (22b) | 30 | 4 | 0.9999 | $133 \pm 4$ | 3 | $<8$ $(3.7 \pm 3.7)$ | | $<0.6$ |
| (22c) | 30 | *g* | | $70.6 \pm 0.6$ | 1 | | | |
| (22c) | 36 | *g* | | $105 \pm 2$ | 2 | | | |
| (22c) | 42 | *g* | | $155 \pm 4$ | 3 | | | |

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses not significantly different from zero. [e] Reaction by $S_N1$ route at [piperidine] $10^{-1}$M. [f] From ref. 7. [g] From Table 4.

TABLE 4

Temperature dependence of second-order rate constants (l mol$^{-1}$ s$^{-1}$) for the reaction of *N*-(*p*-chlorobenzyl)-5,6,8,9-tetrahydro-7-phenylbisbenzo[*a*,*h*]acridinium (22c) with piperidine in chlorobenzene [a]

| | 30 °C | | | 36 °C | | | 42 °C | | |
|---|---|---|---|---|---|---|---|---|---|
| [Piperidine]/M | $10^5\,k_{obs.}$/s$^{-1}$ | $10^3\,k_2$ | $10^3\,k_2$ [b] | $10^5\,k_{obs.}$/s$^{-1}$ | $10^3\,k_2$ | $10^3\,k_2$ [b] | $10^5\,k_{obs.}$/s$^{-1}$ | $10^3\,k_2$ | $10^3\,k_2$ [b] |
| 0.0032 | 22.8 | 71.2 | | 34.0 | 106 | | | | |
| 0.0064 | 44.8 | 70.0 | 70.6 | 66.0 | 103 | 105 | 101 | 158 | 155 |
| 0.0096 | | | | | | | 145 | 151 | |

[a] Measured under pseudo-first-order conditions in l mol$^{-1}$ s$^{-1}$, this compound reacts exclusively by the $S_N2$ mechanism. [b] Average value.

TABLE 5

Correlation between logarithms of second-order rate constants for the reactions of *N*-substituted benzylpyridiniums (b—e) *versus* those of the corresponding *N*-benzylpyridiniums (a)

| *N*-Substituent | Description | No. of points | $r$ | Equations |
|---|---|---|---|---|
| $p$-$MeC_6H_4CH_2$ | (b) | 7 | 0.991 | $\log k_2(b) = 0.983 \log k_2(a) + 0.23$ |
| $p$-$ClC_6H_4CH_2$ | (c) | 5 | 0.998 | $\log k_2(c) = 0.863 \log k_2(a) - 0.26$ |
| $p$-$MeOC_6H_4CH_2$ | (d) | 4 | 0.985 | $\log k_2(d) = 0.826 \log k_2(a) + 0.11$ |
| 2-Furyl-$CH_2$ | (e) | 4 | 0.9998 | $\log k_2(e) = 1.20 \log k_2(a) + 1.76$ |

## EXPERIMENTAL

M.p.s (uncorrected) were determined on a Kofler hot-stage apparatus. The following compounds were prepared using literature methods: 2-methyl-4,6-diphenylpyrylium tetrafluoroborate (2a), m.p. 250—251 °C (lit.,[8] 248.5—250 °C); 2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]chromenylium tetrafluoroborate (6a), m.p. 178—179 °C (lit.,[7] 175—176 °C); 5*H*-2,4-diphenylindeno[1,2-*b*]pyrylium tetrafluoroborate (7a), m.p. 240—242 °C (lit.,[7] 254 °C); 5,6-dihydro-2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (8a), m.p. 224—225 °C (lit.,[9] 270 °C); 5,6-dihydro-4-phenylindeno[1,2-*b*]benzo[*h*]chromenylium tetrafluoroborate (10a), m.p. 218—220 °C (lit.,[7] 268 °C) (Found: C, 72.0; H, 4.6. $C_{26}H_{19}BF_4O$ requires C, 71.9; H, 4.4%); 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium tetrafluoroborate (11a), m.p. 260—262 °C (lit.,[9] 265 °C); 2-methyl-4,6-diphenylpyridine (2b), m.p. 70—71 °C (lit.,[10] 73 °C); 2-t-butyl-4,6-diphenylpyridine (3b), m.p. 89—90 °C (lit.,[9] 87—88 °C); 2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]quinoline (6b), m.p. 97—98 °C (lit.,[7] 97 °C); 5*H*-2,4-diphenylindeno-[1,2-*b*]pyridine (7b), m.p. 158—159 °C (lit.,[7] 156 °C); 5,6-dihydro-4-phenylindeno[1,2-*b*]benzo[*h*]quinoline (10b), m.p. 178—179 °C (lit.,[7] 158 °C); 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridine (11b), m.p. 190—191 °C (lit.,[9] 166—167 °C).

2-*t-Butyl*-2,4-*diphenylpyrylium Tetrafluoroborate* (3a).—Acetophenone (2.4 g, 0.02 mol), t-butyl styryl ketone [11] (3.8 g, 0.02 mol), and $BF_3{\cdot}OEt_2$ (5.7 g, 0.04 mol, 11.2 ml) were heated at 100 °C for 4 h and poured into $Et_2O$ (100 ml) to give the *pyrylium salt* as yellow needles (3.9 g, 52%), m.p. 224—225 °C (decomp.) (Found: C, 66.8; H, 5.3. $C_{21}H_{21}BF_4O$ requires C, 67.0; H, 5.6%).

2-t-*Butyl*-5H-4-*phenylindeno*[1,2-b]*pyrylium Tetrafluoroborate* (5a).—Indan-1-one (1.3 g, 0.01 mol), t-butyl styryl ketone [11] (2.8 g, 0.015 mol), and $BF_3{\cdot}OEt_2$ (2.8 g, 0.02 mol, 5.6 ml) were heated at 100 °C for 2 h and poured into $Et_2O$ (30 ml) to give the *pyrylium salt* (3.0 g), m.p. 194—195 °C, which formed yellow prisms (2.4 g, 63%) (from EtOH), m.p. 197—198 °C (Found: C, 68.0; H, 5.4. $C_{22}H_{21}BF_4O$ requires C, 68.1; H, 5.5%).

4-*Phenylbisindeno*[1,2-b]*pyrylium Tetrafluoroborate* (9a).—Indan-1-one (0.65 g, 0.005 mol), 2-benzylideneindan-1-one [12] (2.2 g, 0.01 mol), HOAc (10 ml), and $BF_3 \cdot OEt_2$ (2.8 g, 0.02 mol, 5.6 ml) were refluxed for 2 h. The *pyrylium salt* separated as yellow prisms (1.0 g, 47%), m.p. 258—260 °C (Found: C, 71.5; H, 4.3. $C_{25}H_{17}BF_4O$ requires C, 71.5; H, 4.1%).

2-*t-Butyl*-5H-*indeno*[1,2-b]*pyridine* (5b).—The pyrylium (5a) (1.0 g, 0.0026 mol), 35% aqueous $NH_4OH$ (0.3 ml), and $Et_2O$ (30 ml) were stirred at 20 °C for 36 h. The solution was washed with $H_2O$, dried ($MgSO_4$), and treated with HCl in $Et_2O$. The *hydrochloride* (0.55 g), m.p. 196—198 °C, crystallised from $Me_2CO$–$Et_2O$ as needles (0.4 g, 46%), m.p. 197—198 °C (Found: C, 78.4; H, 6.3; Cl, 10.4; N, 4.1. $C_{22}H_{22}ClN$ requires C, 78.7; H, 6.6; Cl, 10.6; N, 4.2%). The hydrochloride (0.33 g, 0.001 mol) treated with 20% $NaHCO_3$ (10 ml) gave the *pyridine* (0.2 g, 67%) as a viscous oil (Found: C, 87.8; H, 7.1; N, 4.8. $C_{22}H_{21}N$ requires C, 88.3; H, 7.1; N, 4.7%).

4-*Phenylbisindeno*[1,2-b]*pyridine* (9b).—The pyrylium (9a) (0.4 g, 0.001 mol), EtOH (5 ml), and 35% aqueous $NH_4OH$ (0.5 ml) were stirred at 20 °C for 0.5 h. HOAc (0.5 ml) was added and the mixture was refluxed for 1 h and cooled to give the *pyridine* (0.3 g) which crystallised from HOAc–$H_2O$ as prisms (0.2 g, 60%), m.p. 190 °C (sub.) (Found: C, 90.7; H, 5.3. $C_{27}H_{17}N$ requires C, 90.6; H, 5.2%).

*Preparation of Pyridiniums.—Method A.* Equivalent amounts of amine (0.0026 mol) and $Et_3N$ (0.0026 mol) were added to the pyrylium (0.0026 mol) suspended in $Et_2O$ (30 ml). The resulting mixture was stirred at 20 °C for 12 h. The solid product was filtered off and recrystallised.

*Method B.* The appropriate amine (0.001 mol) and $Et_3N$ (0.001 mol) were added to the pyrylium (0.001 mol) suspended in $CH_2Cl_2$ (3 ml). The resulting solution was stirred at 20 °C for 15 min. HOAc (0.06 ml) was added and the mixture stirred for a further 0.5 h. Dilution with $Et_2O$ (25 ml) gave the pyridinium.

*Method C.* The pyrylium (2a) (0.33 g, 0.001 mol), $Et_2O$ (5 ml), and *p*-methoxybenzylamine (0.14 g, 0.001 mol, 0.13 ml) were stirred at 20 °C for 15 min. The pyridinium was filtered off and recrystallised (see Table 1).

*Method D.* To the pyrylium (8a) (0.4 g, 0.001 mol) suspended in $CH_2Cl_2$ (3 ml) at −15 °C was added *p*-methoxybenzylamine (0.12 g, 0.001 mol, 0.13 ml). The resulting red solution was stirred for 5 min, and HOAc (2 drops) added. The solution was stirred at −15 °C for a further 10 min and dropped into $Et_2O$ (20 ml) at 0 °C. The pyridinium was filtered off (see Table 1).

*Kinetic Measurements.*—The kinetics were followed by u.v. spectrophotometry using the procedure already described.[5] In typical runs under pseudo-first-order conditions the concentration of pyridinium was either $1.6 \times 10^{-3}$ or $3.2 \times 10^{-5}$M, while those of piperidine ranged from 0.00032 to 0.24M. Pseudo-first-order rate constants were calculated from the plot of $\ln [a/(a - x)] = \ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time. Second-order rate constants, unless otherwise stated, were calculated from the slope of the plot of $k_{obs.}$ *versus* piperidine concentration. The extinction coefficients at the kinetic wavelength are reported in Table 6.

TABLE 6

Extinction coefficients for pyridinium cations ($\varepsilon_1$) and for the corresponding pyridines ($\varepsilon_2$) at the kinetic wavelength

| Compound | Kinetic λ/ nm | $\epsilon_1$ | $\epsilon_2$ |
|---|---|---|---|
| (13b) | 300 [a] | 25 000 | 7 000 |
| (13c) | 302 [a] | 29 000 | 7 000 |
| (13d) | 300 [a] | 28 000 | 7 000 |
| (13e) | 300 [a] | 27 000 | 7 000 |
| (14b) | 306 | 26 000 [a] | 5 000 [a] |
| | | 22 000 [b] | 4 500 [b] |
| (14c) | 308 [a] | 26 000 | 5 000 |
| (16a) | 345 [b] | 23 500 | 0 |
| (16d) | 345 [b] | 20 000 | 0 |
| (16e) | 345 [b] | 21 000 | 0 |
| (17b) | 356 [b] | 14 500 | 0 |
| (17c) | 356 [b] | 15 500 | 0 |
| (18a) | 346 [b,c] | 32 400 | 7 500 |
| (18d) | 345 [b] | 22 000 | 7 500 |
| (20a) | 383 [b] | 35 000 | 800 |
| (21d) | 362 [b] | 16 000 | 2 000 |
| (22b) | 400 [b] | 20 500 | 0 |
| (22c) | 400 [b] | 14 000 | 0 |

[a] In 2% (v/v) chlorobenzene–ethanol. [b] In chlorobenzene. [c] Ref. 7.

We thank Messrs. Q. Ansari, G. Bashiardes, R. Bhardwaj, P. McDonnell, and R. Moonilal for help with the experimental work, NATO for a travel grant (to G. M.), and the Ministry of Higher Education, the People's Republic of China, for a grant (to Y. X. Ou).

[1/1338 *Received*, 18*th August*, 1981]

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