Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 11.[1] ρ* Plots for the Solvolysis of 1-s-Alkyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium Cations

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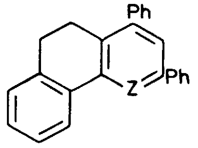
The ρ* values for (1c—h) for (i) solvolysis in trifluoroacetic acid (−5.7), (ii) for solvolysis in pentanol (−1.2), and (iii) for unimolecular reaction with piperidine in chlorobenzene (−3.1) are discussed with respect to (a) the hypothesis that ρ* is a measure of the cation character of the transition state and (b) the S_N2 (intermediate) mechanism. The results are explained for (i) in terms of determining ion-molecule pair dissociation, for (ii) as rate determining S_N2 type solvent attack, and for (iii) as rate-determining ion–molecule pair formation.

The mechanism of the solvolysis of secondary alkyl substrates has long been controversial, particularly as regards the role of the solvent in the process. Such complexities and ambiguities are much less in the gas phase, and recently, the gap between aqueous solution and gas phase has been partially bridged for the $OH^- + CH_3Br$ reaction by using hydrated hydroxide ions in the gas phase: such hydration has indeed large rate lowering effects.[2]

Our recent demonstration [3] that pyridinium leaving groups enable nucleophilic displacement reactions to be studied in non-polar solvents such as chlorobenzene, and that both unimolecular and bimolecular processes are observed there,[4] offers for the first time the possibility of studying the mechanism of dissociation of secondary alkyl substitutes in non-interacting media, and of reinterpreting the existing work in polar solvents.

Bentley and Schleyer [5] have summarised the difficulties in fitting the solvolysis of simple secondary substrates into the S_N1-S_N2 framework, and previous attempted explanations. In a study of the effect of solvents of varying nucleophilicity and ionising power on solvolysis rates, they concluded that 2-adamantyl tosylate (which shows little rate variation with solvent nucleophilicity) reacts by rate-determining ionisation to an intimate ion pair (S_N1), whereas less hindered secondary substrates form solvated ion pairs in the rate-determining step by a mechanism termed 'S_N2 (intermediate)'. Following their development of a scale of solvent nucleophilicities,[6] they demonstrated [7] that the relative solvolysis rates for 2-adamantyl, 1-adamantylmethyl, and 1-bicyclo[2.2.2]octyl tosylates are independent of solvent (over a wide range) whereas the relative rates for 2-adamantyl and 2-propyl tosylates vary by 10^5 from 134 in hexafluoropropan-2-ol to 0.0011 in ethanol. Logarithms of solvolysis rate constants for straight chain secondary alkyl tosylates correlate with σ*; the ρ* values vary with solvent: −9.1 in hexafluoropropan-2-ol, −7.3 in trifluoroacetic acid, −5.2 in 2,2,2-trifluoroethanol, −4.3 in water. They consider that ρ* is a measure of nucleophilic solvent assistance varying from very small in hexafluoropropan-2-ol to large in water, and that there is a gradual change for the secondary alkyl tosylates from S_N1 through S_N2 (intermediate) to the conventional S_N2 mechanism. The Bentley–Schleyer S_N2 (intermediate) mechanism has been supported by kinetic results on decanyl tosylates.[8]

However, at least the initial formulation of an S_N2 (intermediate) mechanism depended on the assumption that the rate-determining step in the solvolysis of 2-adamantyl tosylate, and in the trifluoroacetolysis of all alkyl tosylates, is the formation of intimate ion-pairs without any internal return. Bentley and Schleyer's suggestion that internal return was not appreciable in solvolyses of simple secondary substrates [5,6] has been criticised by Bunnett [9] who demonstrated *ca.* 70% ion return for 2-adamantyl tosylate in three diverse solvents, which supported the earlier interpretation of Winstein.[10] In another recent paper,[11] internal return in the solvolysis of 2-adamantyl tosylate appears to have been proved.



(1)

a; Z = O^+
b; Z = N
c; Z = N^+Pr^i
d; Z = N^+Bu^s
e; Z = N^+-2-pentyl
f; Z = N^+-2-heptyl
g; Z = N^+-3-methyl-2-butyl
h; Z = N^+-3-pentyl

If internal return occurs, the initial ionization cannot be the solvolytic rate-determining step, which is now likely [9] to be the separation of the intimate ion-pair.

Winstein [12] proposed the existence of intimate and solvent-separated ion pairs, and attempted to explain the various behaviour of secondary substrates by involving different rate-determining steps in different situations. Shiner [13] supported this scheme on the basis of α-deuterium kinetic isotope effects: <1.06 was considered characteristic of an S_N2 process, whereas larger than 1.20 was characteristic of rate determination by a dissociated transition state.

In addition to these two main theories, there has been a variety of others: for example Kevill proposes a scale of solvent nucleophilicities [14] and appears to consider the superposition of S_N1 and S_N2 mechanisms.

Aims of Present Work.—We felt it would be useful to measure a series of secondary substrates in the non-interacting solvent chlorobenzene, in two of the solvents typically used for ρ* plots, acetic acid and trifluoroacetic acid, and also in n-pentanol as an example of a much more nucleophilic solvent. As substrates we selected the 1-s-alkyl-5,6-dihydro-2,4-di-

Table 1. 1-Substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates

Compd.	Solvent	M.p. (°C)	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
(1c)	Acetone–ether	145—147	78	72.55	5.7	3.05	$C_{28}H_{26}BF_4N$	78.6	5.65	3.0
(1d)	CH_2Cl_2–ether	130—132	71		*a*		$C_{29}H_{28}BF_4N$			
(1e)	CH_2Cl_2–ether	140—142	77	73.0	6.2	2.8	$C_{30}H_{34}BF_4N$	73.3	6.2	2.8
(1f)	Trituration with light petroleum	100—102	56	73.7	6.7	2.6	$C_{32}H_{34}BF_4N$	74.0	6.6	2.7
(1g)	CH_2Cl_2–ether	205—210	43	73.0	6.2	2.8	$C_{30}H_{30}BF_4N$	73.3	6.2	2.8
(1h)	CH_2Cl_2–ether	147—150	57	73.3	6.2	2.8	$C_{30}H_{30}BF_4N$	73.3	6.2	2.8

[a] Previously reported (lit.,[1] 130—132 °C).

Table 2. U.v. spectral data for 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates

	Chlorobenzene			Pentanol			Acetic acid (6% v/v in EtOH)			Trifluoroacetic acid (4% v/v in EtOH)		
	$\lambda_{max.}$			$\lambda_{max.}$			$\lambda_{max.}$			$\lambda_{max.}$		
Compd.	nm	ε	Kinetic value,[a] ε	nm	ε	Kinetic value, ε	nm	ε	Kinetic value,[b] ε	nm	ε	Kinetic value,[c] ε
(1c)	350	16 800	7 500	350	12 000	11 400	350	13 700	10 600	350	19 200	12 500
(1d)	350	12 600	8 200	350	10 100	8 200	350	10 000	7 700	350	15 700	8 700
(1e)	350	16 800	7 800	350	11 700	10 300	350	17 500	10 300	350	17 900	11 900
(1f)	350	14 700	8 000	350	11 600	11 000	350	10 700	6 500	350	18 000	7 800
(1g)	350	17 400	7 200	350	11 400	9 400	350	18 800	10 900	350	20 100	12 200
(1h)	350	18 300	9 100	350	12 700	11 700	350	17 400	10 900	350	19 700	12 000

[a] Kinetic wavelength, 360 nm. No absorption for the 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoline (1b) at this wavelength. [b] Kinetic wavelength, 360 nm. No absorption for (1b) at this wavelength after dilution with Et_3N–EtOH (see Experimental section). [c] Kinetic wavelength, 360 nm. ε_∞ 1 800 after dilution with Et_3N–EtOH (see Experimental section) due to partial protonation of (1b).

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

Compound[a]	10^3[Piperidine]/mol l^{-1}	$10^5k_{obs}/s^{-1}$
(1c)	0.960	130
	4.80	133
	16.0	149
	32.0	165
(1e)	0.960	302
	4.80	315
	16.0	318
	32.0	304
(1f)	0.960	399
	2.40	404
	4.80	396
	9.60	405
(1g)	0.960	559
	4.80	548
	16.0	530
	32.0	532
(1h)	2.40	526
	9.60	553
	16.0	576
	32.0	578
	48.0	587

[a] Concentration of pyridinium 9.6 × 10^{-5} mol l^{-1}.

Table 4. First-order rate constants (k_1) for the reactions of *N*-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoliniums with piperidine in chlorobenzene at 100 °C

Compound	$10^5k_1/s^{-1}$ [a]
(1c)	129 ± 3
(1e)	311 ± 21
(1f)	398 ± 12
(1g)	553 ± 20
(1h)	539 ± 25

[a] 90% Confidence limit.

phenylbenzo[*h*]quinoliniums (1c—h) which are known[1,15] to react at convenient rates at 100 °C.

Preparation of Compounds.—These were made using standard procedures (see Experimental section) from the pyrylium (1a); details are recorded in Table 1.

Kinetic Measurements.—All the substrates (1c—h) showed strong u.v. absorption at 360 nm (Table 2) whereas the pyridine (1b) does not absorb here. The solvolysis rates in chlorobenzene and n-pentanol were measured at 360 nm by the procedure used previously.[16] However, in trifluoroacetic and acetic acids, pyridine (1b) is protonated, and absorbs at 360 nm: to follow the reaction by u.v. we needed to convert this pyridine into the free base. Therefore the kinetic solutions were diluted to u.v. concentrations with a solution of Et_3N in ethanol before measurement. The presence of Et_3N in the ethanol solution was shown to have no effect on the absorption ($\lambda_{max.}$ or ε) of the pyridinium substrates. This method gave good correlation coefficients.

Using piperidine as a nucleophile in chlorobenzene solvent under pseudo-first-order conditions, good straight lines were obtained to at least 80% completion. The observed rates constants (k_{obs}) for these reactions are recorded in Table 3. Plots of k_{obs} *versus* [piperidine] are straight lines. The k_1 values (intercepts) are given in Table 4; the slopes are not significantly different from zero demonstrating rates independent of piperidine concentration and negligible k_2, conforming to the general pattern that 1-(s-alkyl)pyridiniums react mainly by an S_N1 mechanism.[1,15,17]

Table 5. Solvolysis rate constants for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoliniums in different solvents at 100 °C

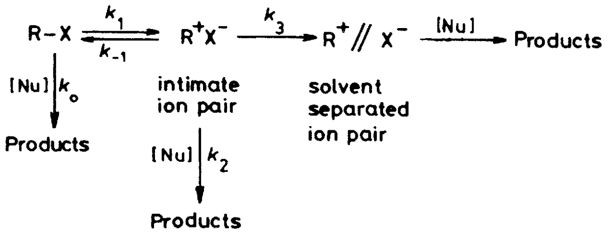
Compd.	Pentanol			Acetic acid			Trifluoroacetic acid		
	$10^5k_{obs}/s^{-1}$ [a]	% Error	Correlation coefficient	$10^5k_{obs}/s^{-1}$ [a]	% Error	Correlation coefficient	$10^5k_{obs}/s^{-1}$ [a]	% Error	Correlation coefficient
(1c)	224 ± 14	6	0.9955	90 ± 2	3	0.9992	0.64 ± 0.04	7	0.998
(1d)	318 ± 13	4	0.9989	130 ± 9	7	0.9978	1.89 ± 0.16	8	0.9967
(1e)	325 ± 29	9	0.9979	224 ± 6	3	0.9996	2.99 ± 0.06	2	0.9998
(1f)	341 ± 15	4	0.9995	278 ± 18	7	0.9980	4.05 ± 0.42	10	0.997
(1g)	420 ± 19	5	0.9990	510 ± 53	10	0.9990	27.27 ± 0.11	4	0.993
(1h)	382 ± 27	7	0.9977	312 ± 12	8	0.9990	9.86 ± 0.57	6	0.999

[a] 90% Confidence limit.

Table 6. ρ* Values in the different solvents

Solvent	Compound						ρ* [a]	Correlation coefficient
	(1c) 7 + log *k*	(1d) 7 + log *k*	(1e) 7 + log *k*	(1f) 7 + log *k*	(1g) 7 + log *k*	(1h) 7 + log *k*		
Chlorobenzene	4.11	4.52 [b]	4.49	4.60	4.74	4.73	−3.1 ± 0.5	0.985
Pentanol	4.35	4.50	4.51	4.53	4.62	4.58	−1.2 ± 0.3	0.970
Acetic acid	3.95	4.13	4.35	4.44	4.71	4.49	−2.9 ± 1.2 [c]	0.955
Trifluoroacetic acid	1.80	2.28	2.48	2.61	3.44	2.99	−5.7 ± 1.2 [c]	0.987

[a] Calculated plotting 7 + log k_1 *vs.* $\Sigma\sigma^*$ (values for σ^* taken from L. S. Levitt and H. F. Widing, *Prog. Phys. Org. Chem.*, 1976, **12**, 119. 90% Confidence limit. [b] From ref. 15. [c] Calculated without including (1g).



Scheme 1.

The solvolysis rate constants for the reactions in pentanol, acetic acid, and trifluoroacetic acid are recorded in Table 5. All reactions were carried out at 100 °C.

Discussion

ρ* *Plots in Pentanol, Acetic Acid, and Trifluoroacetic Acid.*—ρ* Values have been related to the cationic character of the transition state.[18] The ρ* values obtained from the solvolysis of 1-s-alkyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates (1c—h) in these three solvents (Table 5) are in the order expected from Schleyer's previous work. They could indicate assistance from the solvent in the ionization step of the S_N2 (intermediate) mechanism to an extent depending on the nucleophilicity of the solvent. Thus, the reaction in pentanol has ρ* −1.2 consistent with low cationic character in the transition state. By contrast, for the reaction in trifluoroacetic acid (a non-nucleophilic solvent), ρ* −5.7 would indicate a high degree of cationic character in the transition state. Acetic acid (ρ* −2.9) can be interpreted as an intermediate case.

According to Bentley and Schleyer [19] these results would reflect a change in the mechanism from essentially S_N1 to essentially S_N2 through the S_N2 (intermediate) mode. The value reported for ρ* for the trifluoroacetolysis of secondary tosylates is −7.2 at 25 °C,[20,21] which value cannot be directly compared with that (−5.7 at 100 °C) obtained in the trifluoroacetolysis of (1c—h) because of the temperature difference.

ρ* *Plot for Chlorobenzene.*—The reactions of 1-s-alkyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates (1c—h) with piperidine in chlorobenzene are essentially independent of the piperidine concentration. Chlorobenzene is not a nucleophilic solvent, hence the mechanism of the nucleophile-concentration-independent part of these reactions must be S_N1 with cleavage of the C–N bond as the rate-determining step. The ρ* values for the reaction of (1c—h) in chlorobenzene can be obtained from plots of log k_1 (k_1 interception in the k_{obs} *versus* [Nu] plots) *versus* $\Sigma\sigma^*$.

If the unitary mechanism proposed by Bentley and Schleyer were to operate, we should expect that ρ* should be at least as large as that obtained for the non-nucleophilic solvent trifluoroacetic acid. The ρ* value of −3.1 obtained for chlorobenzene appears to be incompatible with either (a) the unitary mechanism, or (b) the hypothesis that ρ* is a measure of the cationic character developed in the transition state of a solvolysis reaction.

Absolute Value of Rates.—Independent of the mechanism, an important difference between solvolyses of (1c—h) and of tosylates occurs in the charge type.

In the neutral tosylates, charge is developed in the transition state of the solvolysis. Hence, the reaction of *e.g.* isopropyl tosylate [5] in trifluoroacetic acid (k 2.49 × 10^{-5} s^{-1}; 25 °C) is faster than that in ethanol (k 0.039 × 10^{-5} s^{-1}; 25 °C). The ionizing power parameters (Y [22] or Y_{OTs} [6]) are $CF_3CO_2H \gg C_2H_5OH$.

By contrast, substrates (1c—h) are themselves positively charged. Therefore the influence of the ionizing power of the solvent will be smaller, and the variation of rates with solvent will depend mainly on the solvent nucleophilicity. The rate constants follow roughly (three points) the solvent nucleophilicity parameters (N and N_{OTs}) [6] and accordingly the reaction in trifluoroacetic acid is much slower than in acetic acid

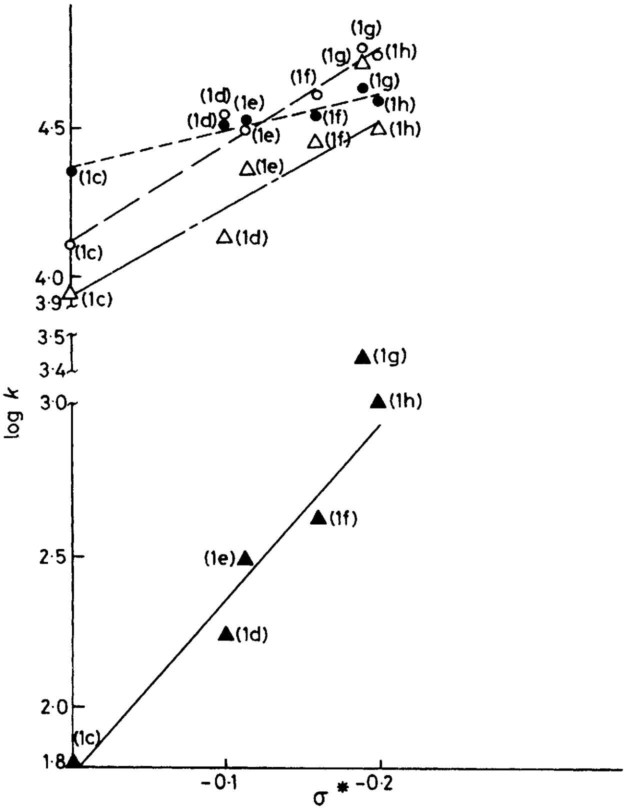


Figure 1. Hammett–Taft plot of solvolysis of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates: ▲, trifluoroacetic acid; △, acetic acid; ●, pentanol; ○, chlorobenzene

or n-pentanol. If a unitary mechanism and solvent assistance proportional to the nucleophilicity of the solvent were to apply, the absolute rate constants for the reactions of (1c—h) with piperidine in chlorobenzene (kinetically independent of piperidine concentration) should be the slowest. In fact, this reaction is much faster (Tables 4 and 5, and Figure 1) than the corresponding one in trifluoroacetic acid; this is incompatible with the unitary mechanism.

Peculiar Behaviour of 1-(3-*Methyl*-2-*butyl*)-5,6-*dihydro*-2,4-*diphenylbenzo*[h]*quinolinium Tetrafluoroborate* (1g).—This substrate reacts faster than expected in all solvents studied, especially in trifluoroacetic acid (see Figure 1). Similar anomalous behaviour reported for the trifluoroacetolysis of 3-methyl-2-butyl tosylate[23] (see Figure 2) has been explained by anchimeric assistance from the neighbouring hydrogen atom[13,19,24] in the rate-determining step. The larger deviation of (1g) from the line (in ρ^* plots), in trifluoroacetic acid is consistent with a greater cationic character in the transition state in the reactions in trifluoroacetic acid.

Consideration of the Results in Terms of the Winstein Scheme.—The results reported in the present paper are incompatible with a unitary mechanism such as that proposed by Bentley and Schleyer for the solvolysis of secondary tosylates. However, they are consistent with a Winstein type mechanism (Schemes 1 and 2) with different rate-determining steps for the different solvents.

The fast reaction in chlorobenzene (ρ^* -3.1), and little anchimeric assistance in (1g), is interpreted in terms of $k_2 \gg k_1$, k_{-1}, k_3, and $k_1 \gg k_0$, *i.e.* irreversible formation of the ion–molecule intermediate as the rate-determining step.

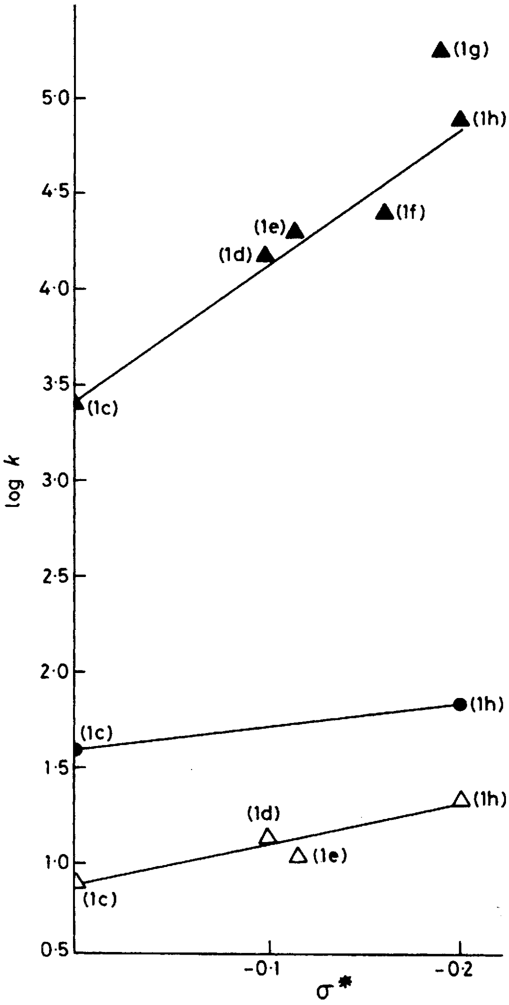
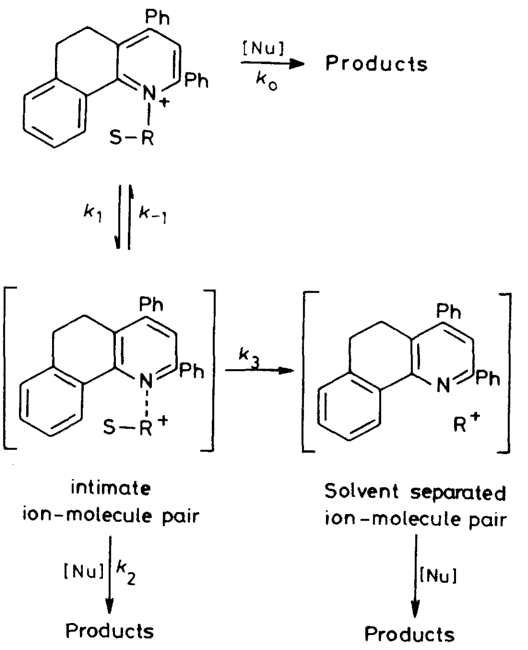


Figure 2. Hammett–Taft plot of solvolysis of tosylates. Data from refs. 5, 21, and 23: ▲, trifluoroacetic acid; △, acetic acid; ●, ethanol

By contrast, for the trifluoroacetolysis [ρ^* -5.7; slow reaction; large anchimeric assistance in (1g)] we believe that both k_0 and k_2 (Scheme 2) are very low. Hence, the rate-determining step is the separation of ion–molecule pair (k_3 in Scheme 2). An analogous step has been proposed by Bunnett[9] as rate determining in the trifluoroacetolysis of several tosylates. The characteristics of the solvolysis in pentanol [ρ^* -1.2; fast reaction; no anchimeric assistance in (1g)] indicate an S_N2-like mechanism (ρ^* -0.74[18] for the solvolysis of primary tosylates in ethanol), in which either k_0 (S_N2 classical or intermediate) or k_2 (S_N2 ion-pair) could be the rate-determining step.

Significance of ρ^* *Plots.*—Conflicting claims about the significance of σ_I and σ^* values for alkyl groups are: (a) that they measure polar effects and can be used to interpret mechanisms;[7,25–27] (b) that they represent steric effects and that the polar effects of alkyl groups are zero.[28–30]

The results of the solvolysis reactions now reported, and the solvolysis of secondary tosylates[7] in different solvents (good correlations with very similar steric requirements) support the contention that σ^* represent polar effects and can be used to interpret mechanisms. That ρ^* is not directly related to the



Scheme 2.

cationic character of the transition state, seems a less likely explanation of our results.

Experimental

M.p.s were determined with a Reichert apparatus and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer model 283B grating spectrophotometer, and ^1H n.m.r. spectra with either a Varian model A-60A, a Varian model EM 360L, or a JEOL model JNM-PMX60 60 MHz spectrometer (Me_4Si as internal standard). U.v. spectra of reactants and products were run on a Pye-Unicam SP8 200 spectrophotometer. For the rate measurements at fixed wavelength a SP6-550 u.v. spectrophotometer was used. Stoppered glass tubes (sealed in the reactions with trifluoroacetic acid), 28 cm high and 13.5 cm in diameter were used as reaction vessels which were placed into the hot blocks (Statim model PROP) for convenient temperature runs.

5,6-Dihydro-2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (1a) was prepared following a literature method, m.p. 275 °C (lit.,[31] 270 °C). 5,6-Dihydro-2,4-diphenylbenzo[*h*]quinoline (1b) was prepared following ref. 31, m.p. 126—127 °C (lit.,[31] 128 °C).

General Procedure for the Preparation of 1-*Substituted* 5,6-*Dihydro*-2,4-*diphenylbenzo*[h]*quinolinium Tetrafluoroborates* (1c–h) (*Table* 1).—5,6-Dihydro-2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (1a) (1.00 g, 0.0023 mol), the amine (0.0023 mol), and Et_3N (0.23 g, 0.0023 mol) were stirred in CH_2Cl_2 (7 ml) for 2 h. AcOH (0.28 g, 0.0046 mol) was added and the mixture stirred for 6 h. After washing the solution with water, precipitation with Et_2O (50 ml) [except for (1f) where light petroleum was used] gave the product (Table 1).

Kinetic Measurements.—Kinetics were followed by u.v. spectrophotometry monitoring the decrease of absorbance of the pyridinium cation at fixed wavelength (360 nm). In the reactions in chlorobenzene and pentanol the procedure already described [16] was used. In typical runs under pseudo-first-order conditions the concentration of pyridinium was 9.6×10^{-5} mol l^{-1}, while those of the nucleophile (when piperidine was used as a nucleophile) varied from 9.6×10^{-4} to 4.8×10^{-2} mol l^{-1}. When trifluoroacetic and acetic acids were used as solvents, a slightly different procedure was followed. The kinetic solutions of pyridiniums (1.6×10^{-3} mol l^{-1}) were diluted to the u.v. concentration (6.4×10^{-5} in the trifluoroacetic case and 9.6×10^{-5} mol l^{-1} in the acetic acid case) using a 4% (v/v) solution of triethylamine in ethanol before any measurement was done.

For all cases, pseudo-first-order rate constants were calculated from the slope of conventional plots of $\ln(a/a - x) - \ln[(\varepsilon_c - \varepsilon_b)/(\varepsilon - \varepsilon_g)]$ (at the kinetic wavelength) *versus* time. For a discussion of errors and precision of measurements see ref. 16*b*.

Such plots were linear to at least 80% completion. The analysis of kinetic data was carried out according to ref. 32.

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