Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 15.[1] Dependence of Mechanism of Solvolysis of Pyridinium Cations on Solvent Character: Evidence from Rates, ρ^* Values, and Product Analysis

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ρ^* Values are reported for solvolyses of a series of 1-(s-alkyl)pyridinium cations in 2,2,2-trifluoroethanol or 1,1,1,3,3,3-hexafluoropropan-2-ol as solvents in the absence of nucleophiles. The corresponding reactions with pyridine, piperidine, or morpholine as nucleophile in chloroform, acetonitrile, 2,2,2-trifluoroethanol, or 1,1,1,3,3,3-hexafluoropropan-2-ol are kinetically first-order (independent of nucleophile concentration); these allow ρ^* to be calculated. ρ^* Values correlate with solvent E_T values except for pentanol and acetic acid, in which cases they are smaller than expected.

Product analysis discloses rearrangement products (derived by hydride shifts) only for solvolysis in non-nucleophilic solvents (trifluoroacetic acid and 1,1,1,3,3,3-hexafluoropropan-2-ol) in the absence of added nucleophilic solvents. The results are interpreted in terms of (a) solvent-assisted solvolysis in nucleophilic solvents, (b) S_N1 cleavage of the C–N bond in the rate-determining step both for the unimolecular reactions in the presence of external nucleophiles, and for solvolysis in 2,2,2-trifluoroethanol, and (c) rate-determining ion–molecule pair dissociation for solvolysis in trifluoroacetic acid or 1,1,1,3,3,3-hexafluoropropan-2-ol.

The role of the solvent in the solvolysis of secondary alkyl substrates has long been controversial.[2–7] Bentley and Schleyer[2] have used ρ^* values as a measure of the cationic character[8] of the transition state and as a measure of the solvent participation in the ionisation step in solvolysis of secondary tosylates.

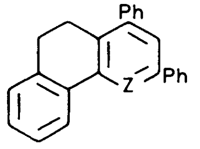
We have demonstrated[9,10] that pyridinium leaving groups enable nucleophilic displacement reactions to be studied in non-polar solvents such as chlorobenzene, and have observed both unimolecular and bimolecular processes. In a recent paper[11] we applied this to study the variations of ρ^* in pyridinium solvolysis reactions, in various solvents. Comparison of the values in non-nucleophilic solvents such as trifluoroacetic acid with those obtained in the apolar non-interacting solvent chlorobenzene seemed incompatible with the unitary 'S_N2 intermediate' mechanism proposed by Bentley and Schleyer.[2,4] Particularly for the non-nucleophilic solvents the results were better explained by a Winstein and Robinson[12] type scheme, with the rate-determining step depending on the solvent.

However, the conclusions in this work[11] implicitly assume the invariability of ρ^* in solvents of different polarity. Furthermore neither in this work, nor in the earlier work of Bentley and Schleyer,[2,4] have any identifications been made of the reaction products from the solvolyses.

Hence, we initiated a systematic study of the kinetically first-order solvolytic reactions of 1-s-alkylpyridinium cations in solvents of a wide range of polarity and nucleophilicity with and without external nucleophiles. We now report this work together with an analysis of the reaction products which has provided new insight into the mechanism. We discuss here the ρ^* values, the absolute rate constants, and the product compositions found in these reactions. These new data complement and extend the conclusions reached in our previous work.[11]

Results

Preparation of Substrates.—As substrates we used 1-s-alkyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates (1c—h), which react at convenient rates[11,13] at 100 °C. They were prepared following reported procedures[11] from the pyrylium cation (1a).



(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

Kinetic Measurements.—All the substrates (1c—h) show strong absorption at 360 nm where the pyridine (1b) does not absorb.[11] The solvolysis rates in 2,2,2-trifluoroethanol and in 1,1,1,3,3,3-hexafluoropropan-2-ol were followed at 360 nm by the previous procedure,[14] and are given in Table 1.

Reactions carried out in the presence of the nucleophile piperidine (chlorobenzene,[11] acetonitrile, and chloroform) or pyridine (2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol) were measured under pseudo-first-order conditions. Good straight lines were obtained to at least 80% completion. The observed rate constants ($k_{obs.}$) for these reactions † plotted against [nucleophile] gave straight lines. The k_1 values (intercepts) are given in Table 2; the slopes are not significantly different from zero, demonstrating the absence of a second-order component. 1-(s-Alkyl)pyridinium cations usually react mainly by an S_N1 mechanism.[10,11,15] All reactions were carried out at 100 °C.

Analysis of Products.—1-(2-Pentyl)- and 1-(3-pentyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cations (1e and 1h) were solvolysed in different solvents and the product mixtures

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† Kinetic data are available as Supplementary Publication No. SUP 23788 (8 pp.). For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

Table 1. Rate constants for the solvolyses of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates (1c—h)

Compound	Pentanol [a] $10^5k_{obs.}/s^{-1}$ [b]	Acetic acid [a] $10^5k_{obs.}/s^{-1}$ [b]	2,2,2-Trifluoroethanol $10^5k_{obs.}/s^{-1}$ [b]	Trifluoroacetic acid [a] $10^5k_{obs.}/s^{-1}$ [b]	1,1,1,3,3,3-Hexafluoropropan-2-ol $10^5k_{obs.}/s^{-1}$ [b]
(1c)	224 ± 14	90 ± 2	1.98 ± 0.07	0.64 ± 0.04	0.24 ± 0.01
(1d)	318 ± 13	130 ± 9	6.73 ± 0.35	1. 89 ± 0.16	
(1e)	325 ± 29	224 ± 6	7.93 ± 0.02	2.99 ± 0.06	2.03 ± 0.08
(1f)	341 ± 15	278 ± 18	12.13 ± 0.43	4.05 ± 0.42	2.96 ± 0.24
(1g)	420 ± 19	510 ± 53	65.74 ± 2.43	27.27 ± 0.11	
(1h)	382 ± 27	312 ± 12	28.13 ± 1.76	9.86 ± 0.57	5.96 ± 0.26

[a] Values taken from ref. 11. [b] 90% Confidence limits (8 runs).

Table 2. First-order rate constants (k_1) for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates with nucleophiles [a] in various solvents at 100 °C

	$10^5k_1/s^{-1}$ [b]			
Compound	Acetonitrile	Chloroform	2,2,2-Trifluoroethanol	1,1,1,3,3,3-Hexafluoropropan-2-ol
(1c)	37 ± 4	257 ± 21	2.07 ± 0.13	0.44 ± 0.02
(1d)	104 ± 1	436 ± 39	8.24 ± 0.50	
(1e)	105 ± 4	680 ± 42	8.77 ± 0.40	2.98 ± 0.10
(1f)	117 ± 6	805 ± 24	10.50 ± 1.00	
(1g)	370 ± 1	1 040 ± 20		
(1h)	222 ± 5	1 020 ± 30	26.00 ± 1.00	6.96 ± 0.50

[a] 10^{-3}—10^{-2}M: piperidine for acetonitrile and chloroform; pyridine for 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol. [b] 90% Confidence limit.

Table 3. ^{13}C Chemical shifts (p.p.m.) of reaction mixtures obtained in various solvents

			Products [a]							
	Starting material		$CH_3CH_2\underset{3}{C}H{-}\underset{2}{C}H_2\underset{1}{C}H_3$			$\underset{1}{C}H_3\underset{2}{C}H{-}\underset{3}{C}H_2\underset{4}{C}H_2\underset{5}{C}H_3$				
Solvent	Compound	*N*-substituent	C-1	C-2	C-3	C-1	C-2	C-3	C-4	C-5
Acetic acid	(1e)	2-Pentyl				20.1	70.8	37.3	17.9	12.9
	(1h)	3-Pentyl	8.5	25.8	76.9					
2,2,2-Trifluoroethanol	(1e)	2-Pentyl				18.7	78.5	38.3	18.4	13.3
	(1h)	3-Pentyl	8.9	25.7	85.0					
Trifluoroacetic acid	(1e) [b]	2-Pentyl	8.5(52)	26.2(64)	84.9(26)	18.7(100)	78.9(81)	37.5(79)	18.2(73)	12.8(71)
	(1h) [b]	3-Pentyl	8.5(76)	26.2(81)	84.9(30)	18.7(100)	78.9(94)	37.5(89)	18.2(81)	12.8(78)
1,1,1,3,3,3-Hexafluoro-propan-2-ol	(1e) [b]	2-Pentyl	8.4(45)	25.4(70)	87.4(24)	18.8(100)	81.3(80)	38.6(76)	18.3(70)	13.6(69)
	(1h) [b]	3-Pentyl	8.4(50)	25.4(75)	87.4(25)	18.8(100)	81.3(92)	38.6(83)	18.3(78)	13.6(73)

[a] 5,6-Dihydro-2,4-diphenylbenzo[*h*]quinoline was present in all the mixtures. [b] Relative intensities (%) in parentheses.

were analysed by ^{13}C n.m.r. (Table 3) and g.l.c.–mass spectrometry. Assignments of ^{13}C peaks were made on the basis of chemical shift considerations, and of off-resonance-decoupled and ^{13}C multiplicity spectra.

We discuss first reactions without an external nucleophile. No rearrangement products were observed with acetic acid or 2,2,2-trifluoroethanol as solvent. Thus, the 1-(2-pentyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cation (1e) gave only 2-pentyl acetate and 2-pentyl 2,2,2-trifluoroethyl ether, respectively. Olefin (elimination reaction) was not detected by ^{13}C, but was found by g.l.c.–mass spectrometry. Similarly, the 1-(3-pentyl) derivative (1 h) gave only the corresponding 3-pentyl acetate and 3-pentyl ether, respectively (Table 3).

With less nucleophilic solvents, *i.e.* trifluoroacetic acid and 1,1,1,3,3,3-hexafluoropropan-2-ol, analogous reactions gave mixtures (*ca.* 50%) of rearrangement and non-rearrangement products. The reactions were followed with time: the ratio of the two products was constant. Thus, solvolyses of 1-(2-pentyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium (1e) in trifluoroacetic acid and in 1,1,1,3,3,3-hexafluoropropan-2-ol gave mixtures of 2-pentyl and 3-pentyl trifluoroacetates, and of 2-pentyl and 3-pentyl 1,1,1,3,3,3-hexafluoroisopropyl ethers, respectively. Similar reactions carried out starting from the 1-(3-pentyl) derivative (1h) afforded mixtures identical with those formed from the 1-(2-pentyl) analogue (see Table 3 and Figure 1).

We confirmed these results by g.l.c.–mass spectrometric studies, which led to conclusions in complete agreement with those from the ^{13}C studies. Thus, the solvolysis of (1e) and (1h) in hexafluoropropan-2-ol each gave mixtures of rearrangement and non-rearrangement products (hexafluoroisopropyl ethers), together with some pent-2-ene (elimination reaction). The fragmentation patterns of the isomeric products obtained from the 2-pentyl derivative (1e) are presented in Table 4. The 3-pentyl ether exhibited characteristic fragment ions at *m*/*z* 209 and 181 corresponding to $M^+ - C_2H_5$ and further loss of C_2H_4, whilst the 2-pentyl ether showed ions at 223 and 195 corresponding to $M^+ - CH_3$ and $M^+ - C_3H_7$. The same results were observed from the 3-pentyl derivative (1h). It was shown by ^{13}C studies that after treatment of 3-pentyl trifluoroacetate (obtained by reaction of pentan-3-ol with trifluoroacetic anhydride) with trifluoroacetic acid at 100 °C the starting material (3-pentyl trifluoroacetate) could be recovered without the formation of any 2-pentyl trifluoroacetate.

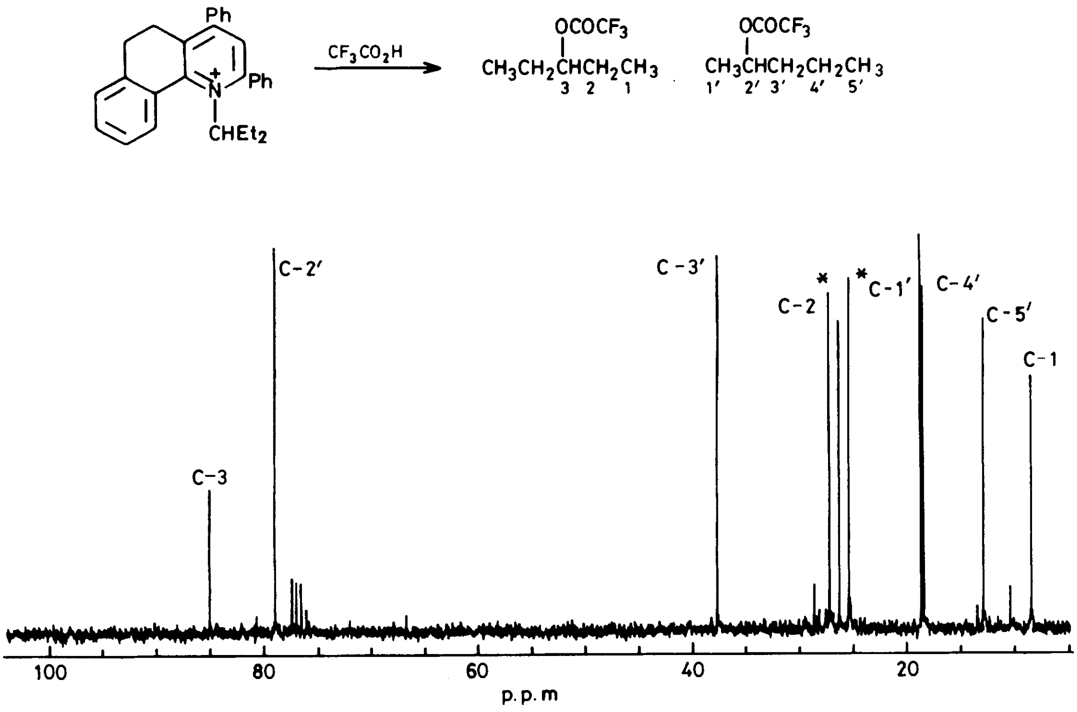


Figure 1. ^{13}C N.m.r. spectrum of the reaction mixture from the solvolysis of 3-pentyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborate in trifluoroacetic acid. The spectrum for the solvolysis of the 2-pentyl derivative was analogous. Asterisks denote aliphatic carbon signals due to the presence of 5,6-dihydro- 2,4-diphenylbenzo[*h*]quinoline in all the mixtures

Table 4. G.l.c. data [a] and major mass spectral fragmentation pattern of the reaction mixture from solvolysis of 2-pentyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium (1e) in 1,1,1,3,3,3-hexafluoropropan-2-ol

	3-Pentyl 1,1,1,3,3,3-hexafluoroisopropyl ether (retention time 672 s)		2-Pentyl 1,1,1,3,3,3-hexafluoroisopropyl ether (retention time 713 s)	
Ion	*m/z*	Intensity (%)	*m/z*	Intensity (%)
$M - 15$			223	5.0
$M - 29$	209	100		
$M - 43$			195	100.0
M − 57	181	40		

[a] Conditions: 2 m × 0.25 in 3% OV-275 on 100—200 Chromosorb W-AW column, flow rate 30 ml min^{-1}, helium carrier gas.

Table 5. G.l.c. data [a] for the retention of 2-pentyl- and 3-pentyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cations (1e and h) in chlorobenzene with piperidine

Peak no.	Compounds	From (1e) t_R	From (1h) t_R
1	Pent-2-ene	48	48
2	Chlorobenzene	191	191
3	*N*-(2-Pentyl)piperidine	542	
	N-(3-Pentyl)piperidine		527
4	5,6-Dihydro-2,4-diphenylbenzo[*h*]quinoline	1 960	1 960

[a] Conditions: 2 m × 0.25 in 3% SP 2100 on 100—120 Supelcoport, flow rate 30 ml min^{-1}, helium carrier gas.

Table 6. Major mass spectral fragmentation patterns of *N*-(2-pentyl)- and *N*-(3-pentyl)-piperidine

	N-(2-Pentyl)piperidine		*N*-(3-Pentyl)piperidine	
Ion	*m/z*	Intensity (%)	*m/z*	Intensity (%)
M	155	1.5	155	1.3
$M - 15$	140	11.3		
$M - 29$			126	100.0
$M - 43$	112	100.0		

Similarly, after 2-pentyl 1,1,1,3,3,3-hexafluoroisopropyl ether (obtained by Williamson's synthesis from sodium 1,1,1,3,3,3-hexafluoroisopropoxide and 2-bromopentane) has been treated with hexafluoropropan-2-ol at 100 °C, the ^{13}C spectrum confirms the presence of only 2-pentyl 1,1,1,3,3,3-hexafluoroisopropyl ether (no isomerisation). Reactions in the presence of external nucleophile were kinetically first-order. The products of these reactions were studied by g.l.c.–mass spectrometry. No rearrangement products were detected in any case. In particular, g.l.c. traces of the 2-pentyl compound (1e) and the 3-pentyl derivative (1h), in chlorobenzene in the presence of piperidine, each gave four peaks, assigned in Table 5. The corresponding mass spectrometric data from peak 3 are presented in Table 6. The fragmentation patterns of the isomeric products obtained in the two reactions were distinctive and characteristic. Whereas both isomers displayed the molecular ion at *m/z* 155, the 2-pentyl derivative exhibited characteristic fragment ions at *m/z* 140 and 112 corresponding to $M^+ - CH_3$ and $M^+ - C_3H_7$, whilst the 3-pentyl derivative showed *m/z* 126 ($M^+ - C_2H_5$) as the only ion with *m/z* > 100.

The same results were obtained in the solvolysis in hexafluoropropan-2-ol. In the presence of morpholine as nucleophile, the 2-pentyl derivative (1e) gave a non-rearrangement product, *N*-(2-pentyl)morpholine, which showed peaks at *m/z* 157 (M^+), 142 ($M^+ - CH_3$), and 114 ($M^+ - C_3H_7$), whilst the 3-pentyl derivative (1h) showed *m/z* 157 (M^+), and 128 ($M^+ - C_2H_5$) due to *N*-(3-pentyl)morpholine.

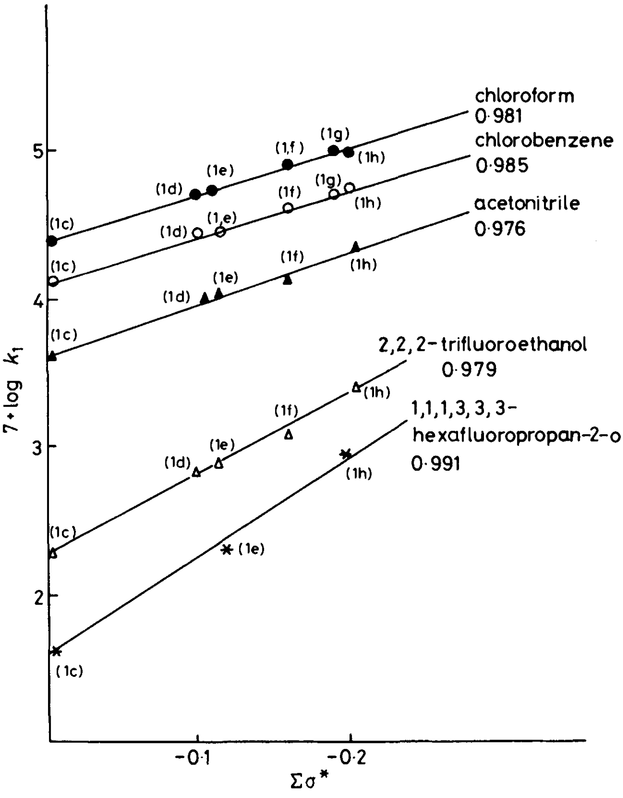


Figure 2. Plot of Σσ* *vs.* 7 + log k_1

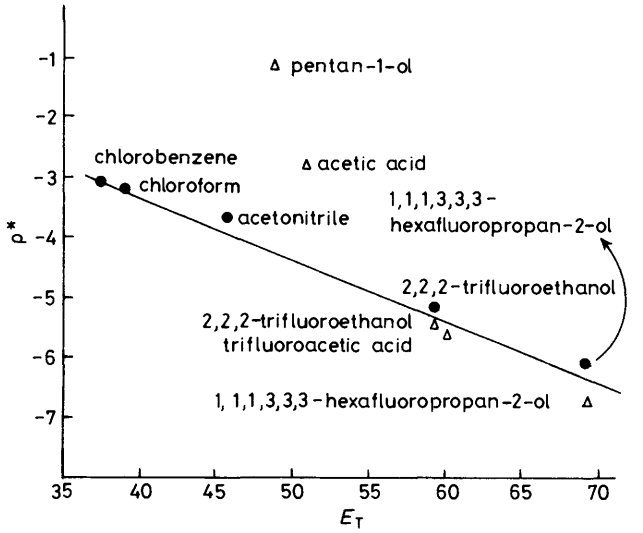


Figure 3. Plot of ρ* *vs.* E_T (solvent polarity parameter of Dimroth) for solvolysis in the presence (●) and in the absence of an external nucleophile (△)

Discussion

ρ Plots for Reactions in the Presence of an External Nucleophile.*—The behaviour of reactions with an external nucleophile is essentially independent of the nucleophile concentration. As many of the solvents used in these reactions are non-nucleophilic, the nucleophile-concentration-independent part of these reactions must be S_N1, with cleavage of the C–N bond as the rate-determining step, at least for chlorobenzene, chloroform, and acetonitrile.

The ρ* values for the reactions of (1c—h) in the various solvents are obtained from plots of 7 + log k_1 (k_1 is the intercept in the $k_{obs.}$ *vs.* [Nu] plots) *vs.* Σσ*[16] (Figure 2). The value of ρ* varies with the polarity of the solvent, being small (absolute values) for apolar solvents [chlorobenzene (−3.1) and chloroform (−3.2)] and increasing with the polarity of the solvent [acetonitrile (−3.6), 2,2,2-trifluoroethanol (−5.2), and 1,1,1,3,3,3-hexafluoropropan-2-ol (−6.1)]. Indeed ρ* for these reactions correlates well with E_T (solvent polarity parameter of Dimroth)[17] (Figure 3), indicating that the C–N bond is broken to a greater extent (more cationic character) in the transition states with the more polar solvents.

According to the Hughes and Ingold theory[18] of solvent effects on rates of nucleophilic substitutions, the reaction rate for a positively charged substrate with a neutral nucleophile decreases with increasing solvent polarity for both the unimolecular and the bimolecular mechanism.[18,19] This agrees with our observations. Charge is more localised in the starting material than in the transition state, and the more localised charge is stabilised by more polar solvents. A more product-like transition state (C–N bond broken to a larger extent) in these polar solvents explains the correlation between ρ* (cationic character of the transition state) and E_T (polarity of the solvent).

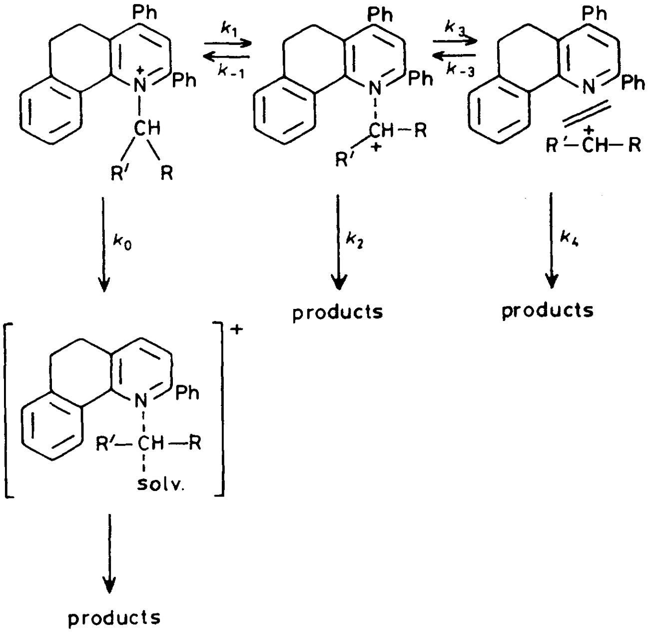
ρ Plots for Solvolysis without an External Nucleophile.*—The ρ* values for solvolyses in solvents of very different nucleophilicity and polarity show qualitative dependence on the polarity of the solvent similar to that found for ρ* in reactions in the presence of an external nucleophile. However, the correlation between ρ* values and E_T (Figure 3) shows two remarkable deviations.

Reactions in pentanol and acetic acid have ρ* values (−1.2 and −2.9, respectively) smaller, and absolute rate constants larger than expected according to the polarity of the solvent (E_T). This fact, in agreement with the observations of Bentley and Schleyer,[2,4] is explained by an associated S_N2 process in which the solvent is behaving as the nucleophile.

The reactions in 2,2,2-trifluoroethanol show very small differences in rate constants in the presence (Table 2) and in the absence (Table 1) of pyridine as external nucleophile. The ρ* value is slightly less negative in the first case (−5.2 *vs.* −5.5) but the difference between the two values is within experimental error. Hence, the mechanism probably involves in both cases irreversible cleavage of the C–N bond as rate-determining step (pure S_N1).

Solvolysis in the non-nucleophilic solvent 1,1,1,3,3,3-hexafluoropropan-2-ol shows a ρ* value in the presence of pyridine of −6.9, which is more negative than that (−6.1) found in the absence of pyridine. Significantly the reactions in the absence of pyridine as external nucleophile are slower than in its presence (Tables 1 and 2). In the presence of nucleophile the ρ* value is that (−6.1) expected for an S_N1 mechanism with cleavage of the C–N bond as the rate-determining step. The reactions in the absence of external nucleophile are explained by supposing the separation of the intimate ion–molecule pair initially formed to be the rate-determining step. Bunnett,[5] supporting an early interpretation by Winstein,[20] has proposed a similar mechanism, based on oxygen scrambling (ion-pair return) found in solvolysis of secondary tosylates in very non-nucleophilic solvents like trifluoroacetic acid.

Interpretation of the Product Analysis.—All the solvolyses in 2,2,2-trifluoroethanol and in acetic acid, both in the presence and in the absence of external nucleophile, showed no rearrangement products. For 2,2,2-trifluoroethanol as solvent, the results are explained by fast attack of solvent or added



Scheme.

nucleophile on the intimate ion–molecule pair irreversibly formed in the rate-determining step (in good agreement with the kinetic results). An ion–molecule pair intermediate has been proposed in the rearrangement of *N*-(α-methylallyl)- to *N*-(γ-methylallyl)pyridinium cations.[21] The lack of rearrangement in the reactions in acetic acid was expected in the light of the kinetic results and the proposed partial S_N2 (or S_N2 intermediate) mechanism.

Solvolyses in trifluoroacetic acid and in 1,1,1,3,3,3-hexafluoropropan-2-ol in the absence of external nucleophiles gave mixtures of rearrangement and non-rearrangement products. This fact provides evidence for the involvement of free carbocations in the solvolyses in trifluoroacetic acid and hexafluoropropan-2-ol. Fast attack by the solvent on a solvent-separated ion–molecule pair or on a free ion (formed in the rate-determining step) explains the preparative and kinetic results.

2,3-Hydride shifts between isomeric secondary carbocations are very fast ($\Delta G^{\ddagger} \leqslant 6$ kcal); for isomerisation to tertiary ions the barrier is much higher (*ca.* 18 kcal).[22]

Conclusions

The value of ρ^* clearly reflects polar effects in the transition state and is thus useful for interpreting mechanism.[16,23–25] However, such interpretations must be made cautiously because the absolute values of ρ^* also depend on the polarity of the solvent (Figure 3), and on other factors such as the nucleophilicity of the solvent and reaction type.

The present kinetic and product analysis results can be interpreted in terms of an ' S_N2 intermediate,' or just an S_N2 mechanism, for solvolyses in nucleophilic solvents such as pentanol and acetic acid ($k_0 > k_1$, Scheme). A pure S_N1 mechanism, with cleavage of the C–N bond as the rate-determining step, is considered to apply for solvolysis in 2,2,2-trifluoroethanol and for all the reactions performed in the presence of an external nucleophile ($k_0 < k_1 < k_2$ in the Scheme).

By contrast, the separation of the initially formed ion–molecule pair is probably the rate-determining step for solvolyses in very non-nucleophilic solvents such as trifluoroacetic acid and 1,1,1,3,3,3-hexafluoropropan-2-ol ($k_2 \ll k_3 < k_4$, k_1, and k_{-1} in the Scheme).

Experimental

U.v. spectra of reactants and products were run on a Pye-Unicam SP 8-200 spectrophotometer. For the rate measurements at fixed wavelength, a Pye Unicam SP 6-500 u.v. spectrophotometer was used. Sealed glass tubes (28 cm long, 13.5 mm diameter) were used as reaction vessels. They were placed in hot blocks (Statim Model PROP) for temperature control (±1 °C). ^{1}H N.m.r. and ^{13}C n.m.r. spectra were measured with a Varian EM 360L instrument, or a JEOL FX 100 or Nicolet NT-300 spectrometer, respectively (Me_4Si as internal standard).

G.l.c.-linked mass spectra were recorded by using an A.E.I. MS-30 mass spectrometer (with Kratos DS-55 data system) interfaced to a Pye 104 gas chromatograph. The column packings employed were 3% SP-2100 on 100—120 Supelcoport, 3% OV-275 on 100—200 Chromosorb W-AW, and 3% SP-2250 DB on 100—200 Supelcoport (2 m × 0.25 in glass columns; helium as carrier gas at flow rates as specified).

Kinetic Measurements.—Kinetics were followed by u.v. spectrophotometry, monitoring the decrease of absorbance of the pyridinium cation at fixed wavelength (360 nm), using the procedure already described.[11] In typical runs under pseudo-first-order conditions the concentration of pyridinium cation was 9.6×10^{-5}M when acetonitrile and chloroform were used as solvents; that of nucleophile (piperidine) varied from 9.6×10^{-4} to 4.8×10^{-3}M.

When trifluoroethanol and hexafluoropropan-2-ol were used as solvents, a slightly different procedure was followed. The solutions of pyridinium cation (1.6×10^{-3}M) were diluted to the concentration required for u.v. measurement (6.4×10^{-5}M) with ethanol. The concentration of nucleophile (pyridine) varied from 6.4×10^{-4} to 6.4×10^{-3}M. All pseudo-first-order rate constants were calculated from the slope of plots of $\ln[a/(a - x)] = \ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time. Such plots were linear to at least 80% completion.

Solvolysis Procedures by ^{13}C *N.m.r.*—Products were studied by sealing 200 mg (4×10^{-4} mol) of (1e) or (1h) in 0.25 ml of the corresponding solvent in an n.m.r. tube, heating for 17 h at 100 °C and then observing the spectrum (Table 3).

Solvolysis of the Cations (1e) *and* (1h) *in Hexafluoropropan-*2-*ol.*—Compound (1e) or (1h) (0.5 g, 0.001 mol) was heated with hexafluoropropan-2-ol (2 ml) in a sealed tube at 100 °C for 17 h. Trituration of the mixture with ether (2 ml) afforded the quinolinium tetrafluoroborate (0.4 g, 94%), m.p. 224—226 °C. The solvents were removed to give a mixture of 2-pentyl and 3-pentyl 1,1,1,3,3,3-hexafluoroisopropyl ethers, together with pent-2-ene as shown by g.l.c.–mass spectrometry (g.l.c. conditions: 3% OV-275 column, flow rate 30 ml min^{-1}) (see Table 4).

Reactions of the Cations (1e) *and* (1h) *with Morpholine in Hexafluoropropan-*2-*ol.*—Compound (1e) or (1h) (0.5 g, 0.001 mol) in hexafluoropropan-2-ol (2 ml) and morpholine (0.26 g, 0.003 mol) was heated in a sealed tube at 100 °C for 17 h. Trituration of the mixture with ether (2 ml) afforded the quinolinium tetrafluoroborate (0.4 g, 94%). The solvents were removed to give a mixture of 2-pentyl and 3-pentyl 1,1,1,3,3,3-hexafluoroisopropyl ethers, *N*-(2-pentyl)morpholine, and pent-2-ene from derivative (1e) and a mixture of 2-pentyl and 3-pentyl 1,1,1,3,3,3-hexafluoroisopropyl ethers, *N*-(3-pentyl)-

morpholine, and pent-2-ene from derivative (1h) as shown by g.l.c.–mass spectrometry (g.l.c. conditions: 3% SP 2250 column, flow rate 30 ml min^{-1}).

Reaction of the Cations (1e) *and* (1h) *with Piperidine in Chlorobenzene*.—Compound (1e) or (1h) (1 g, 0.002 mol) in chlorobenzene (3 ml) and piperidine (0.25 g, 0.003 mol) was heated in a sealed tube at 100 °C for 7 h. G.l.c.–mass spectrometry of the chlorobenzene layer revealed a mixture of pent-2-ene, *N*-(2-pentyl)piperidine, and 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoline from derivative (1e). A mixture of pent-2-ene, *N*-(3-pentyl)piperidine, and 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoline was observed from derivative (1h) (g.l.c. conditions: 3% SP 2100, helium as carrier gas, flow rate 30 ml min^{-1}) (see Tables 5 and 6).

3-*Pentyl Trifluoroacetate*.—Trifluoroacetic anhydride (3 ml) was added to pentan-3-ol (1 g) in cold pyridine (10 ml). Following the vigorous reaction the mixture was poured after 15 s into ice–water (50 ml) and ether (10 ml). More ether was added to form a second layer and the extract was washed with aqueous 2N-hydrochloric acid (2 × 30 ml), water, and aqueous sodium carbonate (5%; 2 × 20 ml). The dried ether layer was distilled giving the ester (1 g, 48%), b.p. 115 °C; δ_H ($CDCl_3$) 0.95 (t, 6 H, $2CH_3$), 1.70 (q, 4 H, $2CH_2$), and 5.00 (qq, 1 H, CH); δ_C ($CDCl_3$) 8.6 (C-1), 26.3 (C-2), and 84.3 (C-3).

2-*Pentyl* 1,1,1,3,3,3-*Hexafluoroisopropyl Ether*.—1,1,1,3,3,3-Hexafluoropropan-2-ol (10 g, 0.06 mol) was dissolved in diethyl ether (10 g) and cautiously treated with metallic sodium (1.4 g, 0.06 mol) over 30 min; the mixture was then refluxed until the sodium had completely disappeared. 2-Bromopentane (9 g, 0.06 mol) was added and the mixture heated in a steam-bath for 20 h. Fractionation gave the ether (2.8 g, 20%), b.p. 70—72 °C; δ_H ($CDCl_3$) 1.2 (t, 3 H, CH_3), 1.9 (m, 7 H, CH_3, $2CH_2$), and 4.0—5.1 (m, 2 H, 2CH); δ_C ($CDCl_3$) 13.7 (C-5), 18.3 (C-4), 18.9 (C-1), 38.6 (C-3), and 81.4 (C-2); *m/z* 238 (M^+), 223 (5%, $M^+ - CH_3$), and 195 (100%, $M^+ - C_3H_7$).

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