and titrated with 0.002 M NaOAc in HOAc. The reaction of autocatalytic, and therefore the first-order plot is curved downward. The rate given in Table II is the initial rate determined over the first 1% reaction.

Solvolyses in ethanol containing 0.25 M 2,6-lutidine were carried out using the sealed ampule technique. Two-milliliter aliquots were added to 4 mL of HOAc and titrated with 0.01 M $HClO_4$ in HOAc. End points were sharper than when titrations were carried out in ethanol. Triflates **6–8** were quite reactive in ethanol. Therefore sealed ampules were not used. The 2-mL aliquots (withdrawn directly from a volumetric flask) were quenched in cold HOAc and titrated as rapidly as possible.

Solvolyses in hexafluoroisopropyl alcohol containing 3% (by weight) water and 0.05 M 2,6-lutidine were carried out using sealed ampules. One-milliliter aliquots were quenched in 4 mL of HOAc and titrated with 0.01 M $HClO_4$ in HOAc. Solvolysis of mesylate **12** in 97% HFIP (no base) was monitored spectrophotometrically. The kinetic run was initiated by injection of 20 μL of a solution of 8.1 mg of **12** in 1 mL of ether into 3 mL of 97% HFIP. The decrease in absorbance at 265 nm was monitored.

Solvolyses in trifluoroacetic acid, containing 0.2 M sodium trifluoroacetate and 0.5% trifluoroacetic anhydride, were monitored by NMR (90 MHz or 300 MHz). First-order plots of trifluoroacetolyses of **6**, **7**, and **8** were curved upward. Rate data given in Table II for **6** and **7** represent "initial" rate constants calculated from data over approximately 10% reaction. Maximum standard deviations in TFA for **3**, **4**, and **5** are ±7%.

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Registry No. 3, 17231-17-3; **4**, 91190-28-2; **5**, 91190-29-3; **6**, 91190-30-6; **7**, 91190-31-7; **8**, 77902-90-0; **12**, 82027-14-3; **13**-OMs, 926-06-7; **13**-OTs, 2307-69-9; **14**, 91190-32-8; **29**, 78801-85-1; **32**, 51761-43-4; deuterium, 7782-39-0.

Kinetics and Mechanisms of Nucleophilic Displacement with Heterocycles as Leaving Groups. 17.[1] Solvolysis of 14-(Primary alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridiniums: Rates, Identification of Products, Activation Parameters, and a General Discussion of Mechanism

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Abstract: Solvolysis rates are reported for the Me, Et, *n*-Pr, *n*-Pent, *n*-Oct, *i*-Bu, *neo*-Pent, $PhCH_2CH_2$, and $MeOCH_2CH_2$ title compounds in MeOH, EtOH, PentOH, CH_3CO_2H, and CF_3CO_2H. Rate variations with alkyl group structure are far less than the corresponding rate variations for the tosylate solvolyses, and afford no evidence for rate-enhancing participation by β-phenyl or β-methoxy groups in the acridinium solvolyses. The *n*-propyl, *n*-pentyl, and *n*-octyl title compounds solvolyze in CH_3OD and CH_3CO_2D to give mixtures of normal and rearranged products, none of which contain deuterium and which are therefore not formed via olefin intermediates. Methanolysis of the isobutyl title compounds occurs via olefin, but the acetolysis also involves an important nonolefinic pathway yielding isobutyl and *sec*-butyl acetates. Methanolysis products from the neopentyl derivative are heavily deuterated, but acetolysis yields undeuterated neopentyl acetate as well as deuterated *tert*-pentyl acetate. Product proportions calculated using GC/MS were used to deduce the fractions of reactions by various mechanistic pathways. Individual rates are calculated for solvolysis to the various unrearranged and rearranged products. They indicate that normal substitution in MeOH occurs by a classical S_N2 reaction, but that such substitution in AcOH involves ion-pair intermediates. It is concluded that such ion pairs undergo Me and H migration after the rate-determining stage, in competition with substitution. Activation parameters provide further evidence for the mechanistic paths proposed which are discussed in relation to literature data available for the corresponding tosylates.

Winstein described the solvolysis of primary systems (**1**) in terms of direct S_N2 displacement with solvent as nucleophile to yield unrearranged product (**3**) (path a of Scheme I) in competition with path b of Scheme I, a first-order anchimerically assisted heterolysis (**1** → **2**) followed by fast formation of rearranged product (**5**).[2-4] This, the so-called $k_s + k_\Delta$ theory,[4] has been supported inter alia by further work by Winstein.[5,6] However, other workers have denied the existence of anchimeric assistance by H or Me transfer and have interpreted the results in terms of paths a, c, and d of Scheme I.[7-9] In 1966, Nordlander and Schleyer[8] summarized the previous evidence for and against participation in the rate-determining stage; they concluded that none was definitive, but provided new evidence from the 1-adamantanylcarbinyl system which they (and we) consider strongly favors nonparticipation. However, the subject remains controversial; thus, in his review,[3] Harris tentatively decides in favor of the $k_s + k_\Delta$ theory, and Ando[10] and Shiner[11] have presented secondary kinetic isotope effect evidence in favor of participation in neopentyl solvolyses.

Essentially all the available work on the solvolyses of primary alkyl systems has been conducted with negatively charged leaving

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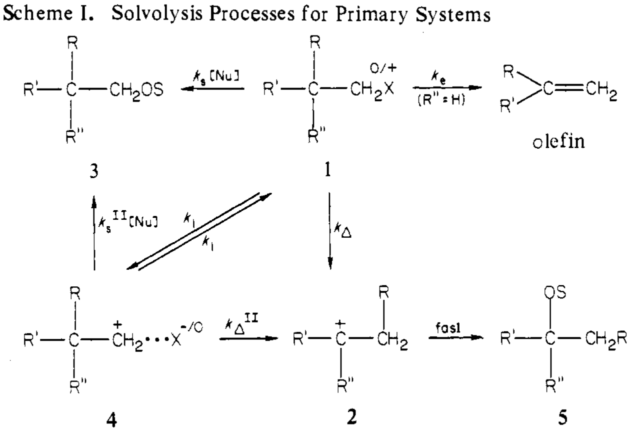
Table I. Preparation of 14-Substituted 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium Tetrafluoroborates (**8**–**17**)

compd	substituent	procedure	yield, %	crystallization solvent	mp, °C	crystal form
8	CH_3	A	61	CH_2Cl_2–EtOH	303	plates
9	C_2H_5	B	67	CH_2Cl_2	254	needles
10	*n*-C_3H_7	B	68	CH_3OH	214[a]	plates
11	*n*-C_5H_{11}	B	60	CH_2Cl_2–pet. ether	178	microcryst
12	*n*-C_8H_{17}	B	52	CH_2Cl_2–pet. ether	147	plates
13	*i*-C_4H_9	B	73	CH_2Cl_2–Et_2O	218	microcryst
14	*neo*-C_5H_{11}	B	75	CH_2Cl_2–Et_2O	182	plates
15	$PhCH_2$	A	69	CH_2Cl_2–Et_2O	184[b]	needles
16	$PhCH_2CH_2$	B	55	CH_2Cl_2–pet. ether	218[c]	microcryst
17	$CH_3OCH_2CH_2$	B	56	CH_2Cl_2–Et_2O	198	microcryst

[a] Lit.[19] mp 213 °C. [b] Katritzky, A. R.; Basinski, W. H.; Ou, Y. X.; Musumarra, G.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1055, report mp 159–160 °C. [c] Lit.[35] mp 190–200 °C.

Scheme I. Solvolysis Processes for Primary Systems



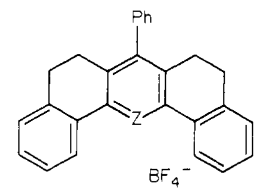
(a) S_N2 path: **1** → **3**. (b) Anchimerically assisted path: **1** → **2** → **5**. (c) Nonparticipatory rearrangement path: **1** → **4** → **2** → **5**. (d) Ionization without rearrangement path: **1** → **4** → **3**. (e) Elimination path: **1** → olefin.

groups.[12] Until recently, the same situation applied to indepth solvolytic studies of *sec*-alkyl systems. However, we recently studied[13,14] the solvolyses of a series of *N*-*sec*-alkyl pyridinium cations in solvents of varying nucleophilicity and basicity. Analysis of the reaction products and comparison of rate variations with those previously reported[15,16] for corresponding tosylates allowed interesting mechanistic conclusions regarding the nature of the transition state and solvent participation in particular.[13] This encouraged us to consider primary alkyl systems, and we now report a complementary study of the solvolyses of a series of primary-alkyl pyridinium cations, extending our earlier work.[17] A major aim of the present work was to gain evidence to decide between the alternative mechanistic interpretations, and on the significance of participation.

We found that 14-(primary alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium tetrafluoroborates solvolyze at convenient rates at 150 °C in a variety of solvents. The present paper reports these rate measurements, together with a study of the products of the solvolysis of representative compounds in methanol and acetic acid, including solvolyses in deuterated solvents. We combine this information to give individual rates for the various types of products formed and show how this information can distinguish between alternative mechanistic pathways. We also report a study of temperature effects on rates and discuss the calculated activation parameters in the light of the mechanistic pathways deduced.

Rate Measurements

The 14-(primary alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium tetrafluoroborates (**8**–**17**) (Tables I and II* (tables marked with an asterisk are available as supplementary material) were prepared from the pyrylium (**6**) by standard methods.[18] The substrates **8**–**17** all show strong UV absorption at 386 nm, whereas



6, Z = O^+	**12**, Z = N^+-*n*-octyl
7, Z = N	**13**, Z = N^+-isobutyl
8, Z = N^+-methyl	**14**, Z = N^+-neopentyl
9, Z = N^+-ethyl	**15**, Z = N^+-benzyl
10, Z = N^+-*n*-propyl	**16**, Z = N^+-(2-phenylethyl)
11, Z = N^+-*n*-pentyl	**17**, Z = N^+-(2-methoxyethyl)

Note: compounds 10A–D are solvolysis products of 10 and are defined in Tables VI and X. Similarly 11A,B refer to products from 11, etc.

the acridine (**7**) is nearly transparent ($\epsilon \leq 1050$) in this region (Table III*). Kinetic runs in 1-pentanol, methanol, ethanol, acetic acid, and trifluoroacetic acid at 150 °C were followed by UV at 386 nm by the previous procedures.[13,19] Good straight lines to at least 80% completion except in trifluoroacetic acid (30% completion) were obtained. Solvolysis rate constants are collected in Table IV.

Solvolysis Rates for Methyl Compounds in Various Solvents. Purely bimolecular reactions by path a (**1** → **3**) are expected for methyl derivatives, and relative rates in different solvents should be dominated by solvent nucleophilicity. This is indeed found for MeOTs;[5,6] rates increase from CF_3CO_2H to CH_3CO_2H to EtOH. For these three solvents, polarity changes inversely with nucleophilicity. Decreasing polarity should moderately decrease the rate of S_N2 reactions of the second charge type (negatively charged leaving group). However, the effect of solvent polarity is clearly far outweighed by solvent nucleophilicity.

Decreasing polarity should moderately increase the rate of S_N2 reactions of the fourth charge type (neutral leaving group); for the solvents utilized for *N*-methylacridinium **8**, polarity and nucleophilicity effects act in concert and give the solvolysis rate variations observed in Table IV: $CF_3CO_2H \ll CH_3CO_2H <$ MeOH < EtOH.

Effect of Structure of Alkyl Group on Rates in Methanol, Ethanol, and Pentanol. The solvolysis rates for ROTs in EtOH show a decrease for R = Me > Et > *n*-Pr > *i*-Bu > *neo*-Pent. In all these cases (except *neo*-Pent) the S_N2 process (path a of

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Table IV. Solvolysis Rate Constants of 14-(Primary alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c,h*]acridinium Tetrafluoroborates at 150 °C

		1-pentanol		ethanol		methanol		acetic acid		trifluoroacetic acid	
compd no.	substituent	10^5k_{obsd} (s^{-1})	corr coeff	10^5k_{obsd} (s^{-1})	corr coeff	10^5k_{obsd} (s^{-1})	corr coeff	10^5k_{obsd} (s^{-1})	corr coeff	10^5k_{obsd} (s^{-1})	corr coeff
8	methyl	*a*		59 ± 16	0.9918	1.78 ± 0.18	0.9941	1.27 ± 0.13	0.9952	$<5 \times 10^{-3}$	
9	ethyl	383 ± 108	0.9908	263 ± 28	0.9950	10.7 ± 0.40	0.9990	2.93 ± 0.06	0.9997	0.022 ± 0.002	0.9966
10	*n*-propyl	354 ± 39	0.9967	276 ± 15	0.9986	8.61 ± 0.40	0.9990	2.01 ± 0.002	0.9998	0.0085 ± 0.0001	0.9971
11	*n*-pentyl	489 ± 119	0.9931	180 ± 9	0.9984	6.38 ± 0.40	0.9969	2.54 ± 0.04	0.9997	*b*	
12	*n*-octyl	267 ± 21	0.9983	55 ± 6	0.9910	4.82 ± 0.83	0.9821	2.05 ± 0.04	0.9996	*b*	
13	isobutyl	391 ± 35	0.9990	68 ± 4	0.9949	5.62 ± 0.20	0.9997	3.63 ± 0.06	0.9997	0.035 ± 0.002	0.9986
14	neopentyl	332 ± 34	0.9988	50 ± 5	0.9976	1.61 ± 0.11	0.9988	5.71 ± 0.26	0.9991	0.44 ± 0.02	0.9981
16	2-phenylethyl	385 ± 24	0.9993	98 ± 7	0.9956	4.08 ± 0.15	0.9994	1.76 ± 0.04	0.9996	0.047 ± 0.002	0.9985
17	2-methoxyethyl	323 ± 82	0.9924	16 ± 5	0.9870	2.87 ± 0.09	0.9991	0.65 ± 0.01	0.9995	0.011 ± 0.001	0.9995

[a] Not soluble. [b] Not measured.

Scheme I) should dominate, and the rate decrease is due to the well-known increasing steric hindrance in the transition state.[2,3,5,6]

For the acridiniums **8–17**, in MeOH, the rates also decrease Et > *n*-Pr > *i*-Bu > *neo*-Pent, but the relative decrease is much smaller and the rate actually increases from Me to Et (Table V). This could arise because steric hindrance is now of considerable importance in the ground state as well as in the transition state,[20] leading to steric acceleration. The increase in steric hindrance in the ground state is particularly important from Me to Et and from *i*-Bu to *neo*-Pent,[20] and it is just at these points when the greatest differences in the behavior of the tosylates are found.

The relative rates for the acridiniums **8–17** in EtOH closely parallel those for the same substrates in MeOH solvent (see Table V). In pentanol, the rates show almost no variation with alkyl group structure.

Effect of Structure of Alkyl Groups on Rates in Trifluoroacetic and Acetic Acids. The solvolysis rates for ROTs in CF_3CO_2H increase for R = Me < Et < *n*-Pr < *i*-Bu < *neo*-Pent. This has been considered[5,6] largely due to a change in mechanism from path a of Scheme I to path b or c; the unimolecular mechanism is greatly encouraged by the high polarity solvent and in one interpretation by anchimeric assistance.

For the acridiniums **8–17** the rates in CF_3CO_2H increase from Me to Et (for the reason discussed above), decrease again for R = *n*-Pr, and then increase markedly. For a neutral leaving group, a highly polar medium shows a smaller preference for an S_N1-type over a S_N2-type mechanism as compared to a negatively charged leaving group. Hence the minimum rate is expected to occur later in the series. However, the rate increase *n*-Pr to *neo*-Pent is comparable to that found in the tosylate series (Table V), implying similar mechanisms.

Both for the tosylates ROTs and for the acridiniums **8–17**, the absolute rates in acetic acid are intermediate between those for the same compounds in EtOH and in CF_3CO_2H. This applies also to the relative rates (Table V); here the pattern for the ROTs is closer in AcOH to that in EtOH, whereas for the acridiniums **8–17** that pattern in AcOH is closer to that found in CF_3CO_2H.

Rates for 2-Phenylethyl and 2-Methoxyethyl Compounds. The 2-phenylethyl derivatives show in most solvents rates which are rather less than those for the ethyl analogues both for the tosylates and for the acridiniums (Table V). The very large relative rate for $PhCH_2CH_2OTs$ in CF_3CO_2H has been ascribed to the importance of anchimeric assistance.[21] The much smaller relative rate for the 2-phenylethylacridinium (**16**) in CF_3CO_2H indicates that such anchimeric assistance is sensibly absent there. A similar conclusion is reached from the rates found for the 2-methoxyethylacridinium (**17**); here no comparison is available for CF_3CO_2H solvent, although work carried out on brosylates[22] in EtOH and AcOH solvents give similar ratios to those found for the $PhCH_2CH_2$ group. An examination of models indicates that participation by the phenyl group in **16** would result in considerable added strain. Rates for the benzyl compound (**15**) were too fast to measure by the technique used.

Identification of Solvolysis Products

Mixtures from solvolyses carried out at 150 °C in sealed tubes for 24 h were subjected to gas chromatography, with mass spectral analysis of the separated components.

Solvolyses in Methanol. The solvolysis products of tetrafluoroborates **10–14** in methanol and in methanol-*d* are recorded in Table VI. Gas chromatographic separation of the reaction mixtures showed that, as expected, the same reaction products were formed in (to within experimental error) the same proportions in both the deuterated and nondeuterated solvents (Table VI).

The individual products were identified by their mass spectra, of which major peaks are given in Tables VII and VIII*. In the case of products **10**A, **11**A, **11**B, and **12**A–E (formed from com-

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Table V. Relative Rates of *N*-(Primary alkyl) Acridiniums and Corresponding Tosylates in Several Solvent Systems

	acridiniums					tosylates[a]		
solvent	*n*-$C_5H_{10}OH$	C_2H_5OH	CH_3OH	CH_3CO_2H	CF_3CO_2H	C_2H_5OH	CH_3CO_2H	CF_3CO_2H
Y^b		-2.03	-1.09	-1.64	1.84	-2.03	-1.64	1.84
N^b		0.09	0.01	-2.05	-4.74	0.09	-2.05	-4.74
substituent								
CH_3		0.2	0.2	0.4	<0.2	2.3	1.1	0.08
CH_3CH_2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$CH_3CH_2CH_2$	0.9	1.0	0.8	0.7	0.4	0.6	0.8	7.5
$CH_3(CH_2)_3CH_2$	1.2	0.7	0.8	0.8				
$CH_3(CH_2)_6CH_2$		0.2	0.4	0.7				
$(CH_3)_2CHCH_2$	1.0	0.3	0.5	1.2	1.6	0.04	0.3	245
$(CH_3)_3CCH_2$	0.8	0.2	0.1	2	23	5.7×10^{-4}	0.1	477
$C_6H_5CH_2$		(fast)		(fast)		165[c]	1550[c]	
$C_6H_5CH_2CH_2$	0.9	0.4	0.4	0.6	2.1	0.24[d]	0.4[d]	1770[d]
$CH_3OCH_2CH_2$	0.8	0.06	0.3	0.2	0.5	0.25[e]	0.3[e]	

[a] From ref 3, p 119. [b] From ref 16a. [c] At 50 °C: from ref 32. [d] From ref 21. [e] From ref 22; these relative rates apply to brosylates.

Table VI. Products from Solvolyses of 14-Alkyl Acridinium Tetrafluoroborates in CH_3OH and CH_3OD at 150 °C: Structures, Proportions, and Retention Times

				CH_3OH			CH_3OD		
compd no.	R	product	product structures	mol %	GC temp, °C	RT, s	mol %	GC temp, °C	RT, s
10	$CH_3CH_2CH_2$	**10A**	$CH_3OCH_2CH_2CH_3$	100	25	105	100	30	107
11	$CH_3(CH_2)_3CH_2$	**11A**	$CH_3OCH_2(CH_2)_3CH_3$	97	30	526	99	30	376
		11B	$CH_3OCH(CH_3)CH_2CH_2CH_3$	3	30	360	1	30	267
12	$CH_3(CH_2)_6CH_2$	**12A**	$CH_3OCH_2(CH_2)_6CH_3$	94	150	1090	89	150	1130
		12B	$CH_3OCH(CH_3)(CH_2)_5CH_3$	1	150	999	4	150	1034
		12C	$CH_3OCH(C_2H_5)(CH_2)_4CH_3$	0.4	150	980	0.3	150	1014
		12D	$CH_2{=}CH(CH_2)_5CH_3$	3	150	549	5	150	551
		12E	$CH_3CH{=}CH(CH_2)_4CH_3$	1	150	583	2	150	592
13	$(CH_3)_2CHCH_2$	**13A**	$CH_3OC(CH_3)_3$	90	50	126	90	30	127
		13B	$(CH_3)_2C{=}CH_2$	10	50	60	10	30	67
14	$(CH_3)_3CCH_2$	**14A**	$CH_3OC(CH_3)_2CH_2CH_3$	43	30	325	48	30	239
		14B	$(CH_3)_2C{=}CHCH_3$	57	30	110	52	30	89

pounds **10–12**) (Table VII), no excess deuterium was found; i.e., the mass spectral patterns were identical with those that would have been formed from the corresponding products formed in CH_3OH. The mass spectra of **10A**, **11A**, **11B**, **12C**, **12D**, and **12E** are well known,[23] and these products were identified by direct

$R{-}O^+$

18a, R = C_3H_7
b, R = C_4H_9
c, R = C_5H_{11}
d, R = C_8H_{17}

$R{-}CH{=}CH{-}CH_2^+$

19a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = *n*-C_3H_7
e, R = *n*-C_4H_9
f, R = *t*-C_4H_9

$CH_3{-}C(=O){-}O{-}\overset{+}{C}H{-}R$

20a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = *n*-C_3H_7
e, R = *n*-C_4H_9
f, R = *n*-C_5H_{11}

$CH_3{-}\overset{+}{O}{=}CH{-}R$

21a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = C_3H_7
e, R = C_4H_9
f, R = C_5H_{11}
g, R = C_6H_{13}

$CH_3{-}\overset{+}{O}{=}C(CH_3){-}R$

22a, R = CH_3
b, R = C_2H_5

comparison of the measured spectra with those previously recorded;[23] very good agreement was found. Compounds **12A** and **12B** were identified as 1- and 2-octyl methyl ether, respectively (no published mass spectral data available); the assignment was based on their highly characteristic fragmentation patterns (β-cleavage to the ether bond). **12A** showed the most abundant ion (in agreement with literature data[24] reported for straight-chain alkyl methyl ethers) at m/z 45 (100) due to $[M^+ - C_7H_{15}]$. **12B** exhibited the most abundant ion at m/z 59 (100) corresponding to $[M^+ - C_6H_{13}]$, proving it to be 2-octyl methyl ether. The unrearranged methyl primary-alkyl ethers **10A** (*n*-propyl methyl ether) and **11A** (*n*-pentyl methyl ether) gave spectra identical with the literature;[23] in accordance, the mass spectrum of **12A** showed the most abundant peak at m/z 45 (100). 3-Octyl methyl ether (**12C**) gave the characteristic ion at m/z 73 (100) due to $M^+ - C_5H_{11}$. The olefins **12D** and **12E** exhibited the molecular ion at m/z 112. 1-Octene (**12D**) and 2-octene (**12E**) gave characteristic ions at m/z 43 (100) and 55 (100), respectively (see Table VII).

The mass spectra of **13A**, **13B**, **14A**, and **14B** are also available,[23] and these products formed in CH_3OH were identified by direct comparison of their mass spectra (Table VIII*) with those in the literature. *tert*-Butyl methyl ether (**13A**) showed the most abundant ion at m/z 73 (100) due to $[M^+ - CH_3]$. 1,1-Dimethylpropyl methyl ether (**14A**) exhibited characteristic ions at m/z 87 and 73 (100) due to $[M^+ - CH_3]$ and $[M^+ - C_2H_5]$, respectively. 2-Methylpropene (**13B**) showed peaks at m/z 56 (M^+) and 41 (100). 2-Methyl-2-butene (**14B**) gave peaks at m/z 70 (M^+) and 55 (100) corresponding to $[M^+ - CH_3]$.

By contrast, products **13A**, B and **14A**, B, when formed from solvolyses in CH_3OD, contained considerable excess deuterium. By comparison of the mass spectra of the products formed in CH_3OD with those obtained in CH_3OH (Table VIII*), it was possible to determine the relative amounts of mono-, di-, and trideuterio content for each fragment ion for the products obtained in CH_3OD. The results are given for some significant fragment ions in Table IX*.

In **13A** (CH_3OBu^t), the *tert*-butyl group has become completely equilibrated, with approximately half the hydrogen atoms exchanged. Allowing for some background, the pattern of peaks found for $[CH_3{-}O^+{=}C(CH_3)_2]$ is not very different from the path expected for complete randomization: 2, 9, 23, 32, 23, 9,

(23) Heller, S. R.; Milne, G.W.A. "EPA/NIH Mass Spectral Base"; National Bureau of Standards: Washington, D.C., 1978; Vol. 1 and Suppl. 1.

(24) Tsang, C. W.; Harrison, A. G. *Org. Mass Spectrom.* **1970**, *3*, 647.

Table VII. Relative Intensities of Major Mass Spectral Fragmentation Peaks of Products Formed in Solvolyses of 14-*n*-Propyl- (**10**), 14-*n*-Pentyl- (**11**), and 14-*n*-Octyl-(**12**) Acridinium Tetrafluoroborates in CH_3OH and CH_3OD at 150 °C

	structure of	products[a]							
m/z	characteristic fragment ion	**10A**	**11A**	**11B**	**12A**	**12B**	**12C**	**12D**	**12E**
129	n-$C_6H_{13}CH{=}O^+{-}CH_3$ (**21g**)					1.6			
115	n-$C_5H_{11}CH{=}O^+{-}CH_3$ (**21f**)						32.4		
112	$C_8H_{16}^{+\cdot}$ isomers				14.7	1.1		5.8	19.1
97	n-$C_4H_9CH{=}CHCH_2^+$ (**19e**)				1.2	1.6		1.5	
84	$C_6H_{12}^{+\cdot}$ isomers				33.4	1.0	5.0	11.3	9.9
83	n-$C_3H_7CH{=}CHCH_2^+$ (**19d**)				18.8	1.0	31.8	18.0	16.2
74	$C_4H_{10}O^{+\cdot}$	12.2				0.4	62.3		
73	$C_2H_5CH{=}O^+{-}CH_3$ (**21c**)		12.8	33.0		1.0	100		
70	$C_5H_{10}^{+\cdot}$ isomers			5.0	24.5	2.4	6.5	54.7	54.8
69	$C_2H_5CH{=}CHCH_2^+$ (**19c**)				24.4	2.3	6.4	31.3	29.7
59	$CH_3CH{=}O^+{-}CH_3$ (**21b**)	0.4	2.3	100	0.5	100	8.3		
57	$C_4H_9^+$				10.6	3.0	10.8	11.9	35.8
56	$C_4H_8^{+\cdot}$ isomers		1.6		37.6	3.3	10.8	68.1	84.6
55	$CH_3CH{=}CHCH_2^+$ (**19b**)		8.6	9.0	22.5	9.7	38.5	84.6	100
45	$CH_3{-}O^+{=}CH_2$ (**21a**)	100	100	42.0	100	6.3	2.3		
43	$C_3H_7^+$			26.1				100	24.6
42	$C_3H_6^{+\cdot}$	2.1	18.2	2.2	15.9	3.9	13.3	71.2	59.0
41	$CH_2{=}CHCH_2^+$ (**19a**)	6.9	10.6	20.1	24.9	8.2	36.2	83.2	83.8

[a] Registry number of mass spectra from ref 23: **10A**, 557-17-5; **11A**, 628-80-8; **11B**, 6795-88-6; **12C**, 54658-02-5; **12D**, 111-66-0; **12E**, 111-67-1.

Table X. Products from Solvolyses of 14-Alkyl Acridinium Tetrafluoroborates in CH_3CO_2H, CH_3CO_2D, and CD_3CO_2D at 150 °C: Structures, Proportions, and Retention Times

				CH_3CO_2H			CH_3CO_2D			CD_3CO_2D		
compd	R	product	product structures	mol %	GC temp, °C	RT, s	mol %	GC temp, °C	RT, s	mol %	GC temp, °C	RT, s
10	$CH_3CH_2CH_2$	**10B**	$CH_3COOCH_2CH_2CH_3$	87	200	193	88	50	342			
		10C	$CH_3COOCH(CH_3)_2$	12	200	133	11	50	222			
		10D	$CH_3CH{=}CH_2$	<1	200	40	<1	50	45			
11	$CH_3(CH_2)_3CH_2$	**11C**	$CH_3COOCH_2(CH_2)_3CH_3$	89	200	839	90	150	725			
		11D	$CH_3COOCH(CH_3)CH_2CH_2CH_3$	8	200	547	7	150	399			
		11E	$CH_3CH{=}CHCH_2CH_3$	2	200	55	2	150	40			
		11F	$CH_2{=}CHCH_2CH_2CH_3$	0.5	200	83	0.3	150	61			
12	$CH_3(CH_2)_6CH_2$	**12D**	$CH_2{=}CH(CH_2)_5CH_3$	7	150	543	10	150	446			
		12E	$CH_3CH{=}CH(CH_2)_4CH_3$	4	150	578	5	150	473			
		12F	$CH_3COOCH_2(CH_2)_6CH_3$	81	150	1436	78	150	1380			
		12G	$CH_3COOCH(CH_3)(CH_2)_5CH_3$	6	150	1317	5	150	1245			
		12H	$CH_3COOCH(C_2H_5)(CH_2)_4CH_3$	1	150	1289	1	150	1218			
		12I	$CH_3COOCH(n\text{-}C_3H_7)(CH_2)_3CH_3$	0.5	150	1275	0.5	150	1204			
13	$(CH_3)_2CHCH_2$	**13B**	$(CH_3)_2C{=}CH_2$	42	200	48	45	200	48	45	200	41
		13C	$CH_3COOC(CH_3)_3$	13	200	187	15	200	221	16	200	165
		13D	$CH_3COOCH(CH_3)CH_2CH_3$	20	200	312	19	200	374	17	200	281
		13E	$CH_3COOCH_2CH(CH_3)_2$	21	200	368	20	200	443	20	200	336
		13F	$(CH_3)_3CCH_2C(CH_3){=}CH_2$	4	200	76	1	200	83	2	200	68
14	$(CH_3)_3CCH_2$	**14B**	$(CH_3)_2C{=}CHCH_3$	68	50	55	84	200	40	84	200	52
		14C	$CH_3COOC(CH_3)_2CH_2CH_3$	15	50	353	3	200	162	4	200	340
		14D	$CH_3COOCH_2C(CH_3)_3$	14	50	581	7	200	433	9	200	560
		14E	$CH_3COOCH(CH_3)CH(CH_3)CH_3$	3	50	484	6	200	345	3	200	464

2%. However, the distribution of the hydrogen atoms in (**13B**) [$CH_2{=}C(CH_3)_2$] is skewed from the random 0.5, 3, 11, 22, 27, 22, 11, 3, 0.5% expected; there is a small excess of the nondeuterated species.

In **14A** [$CH_3OC(CH_3)_2CH_2CH_3$], the pattern is interpreted to show that the two methyl groups have become completely equilibrated with solvent deuterium, but only the CH_2 of the ethyl group. Thus in the *m/z* 87 peak, heavy population is found up to the pentadeuterated species, whereas the *m/z* 73 peak is hexadeuterated.

Similarly in the olefin $(CH_3)_2C{=}CHCH_3$ (**14B**), one methyl group has essentially escaped deuteration as is apparent from the species pattern (Table IX); see especially the heptadeuteration of the molecular ion.

Solvolyses in Acetic Acid. The solvolysis products of tetrafluoroborates (**10** – **14**) in acetic acid, acetic acid-*d* and/or acetic-d_3 acid-*d* are recorded in Table X. The solvolyses of **13** and **14** were examined in all three solvents, and the others in CH_3CO_2H and CH_3CO_2D. In all cases the GC traces showed that the same reaction products were formed in (to within experimental error) the same proportions (Table X).

Our group previously reported[17] that the solvolysis in acetic acid of the 14-(*n*-octyl)acridinium (**12**) (as triflate) gave 1-, 2-, 3-, and 4-octyl acetates in proportions 87:6:4:3. The present work, considered to be more accurate, had disclosed in addition the presence of significant amounts of olefinic products.

Acetic acid-*d* (CH_3CO_2D) heated under the condition of the solvolysis experiments undergoes equilibration between the OD and CH_3 groups as shown by ^{1}H NMR (asymmetric broadening of the CH_3 signal) and mass spectroscopy (CH_3CO^+ peak at *m/z* 43, 44, 45, and 46 in ratio 39:15:22:24), in agreement with previous work.[25]

All the acetates from the solvolysis of **10** – **12** in CH_3CO_2D and also **13D**, **13E**, **14D**, and **14E** showed incorporation of deuterium in the acetyl group (Table XI)*. Significantly, the pattern of deuteration is similar for the products from the same precursor, and furthermore we find approximately that $3[d_0]/[d_1] = [d_1]/[d_2] = [d_2]/3[d_3]$. However, these products showed *no* deuterium incorporation *other* than in the acetyl group; this was

(25) Yamada, N.; Suma, K.; Takeuchi, T. *J. Chem. Soc. Jpn., Pure Chem. Sect.* **1953**, *74*, 1018.

Table XXI. Percentage of Products Formed by Various Reaction Paths in Solvolyses of Alkyl Acridinium Tetrafluoroborates (**10–14**)

		substitution products not via olefin, %				products via olefin, %		
compd	R	unrearranged	one rearrangement	two rearrangements	three rearrangements	rearranged substitution product	olefins a	olefins b
				CH_3OH				
10	$CH_3CH_2CH_2$	100						
11	$CH_3(CH_2)_3CH_2$	97	3					
12	$CH_3(CH_2)_6CH_2$	94	1	0.4			3	1
13	$(CH_3)_2CHCH_2$					90	10	
14	$(CH_3)_3CCH_2$					43	57	
				CH_3CO_2H				
10	$CH_3CH_2CH_2$	87	12				1	
11	$CH_3(CH_2)_3CH_2$	89	8				2	0.5
12	$CH_3(CH_2)_6CH_2$	81	6	1	0.5		7	4
13	$(CH_3)_2CHCH_2$	21	20			13	42	4
14	$(CH_3)_3CCH_2$	15				17	68	

shown by direct study of the corresponding alkyl fragment ions (see Table XII)*.

The mass spectra of all compounds recorded in Tables XIII–XVII* (except **12I**) are known,[23] and the measured spectra were identical with the literature mass spectra. The mass spectra of octyl acetates (**12F–I**) were previously identified in the solvolysis of 14-*n*-octylacridinium (**12**) in acetic acid.[17] Unrearranged primary alkyl acetates **10B**, **11C**, **12F**, **13E**, and **14D** showed characteristic peaks at m/z 43 (most abundant ion), 61, and 73, corresponding to $[CH_3CO]^+$, $[CH_3C(OH)_2]^+$, and $[CH_3COOCH_2]^+$, respectively (Tables XIII–XVII)*.

Of the rearranged alkyl acetates (Tables XIII–XVII*), **10C** (isopropyl), **11D** (2-butyl), and **12G** (2-octyl) showed an m/z peak at 87, due to $[CH_3CO_2CHCH_3]^+$, but no signal at m/z 73. The characteristic peak at m/z 101 $[M^+ - C_5H_{11}]$ in **12H** proves that it corresponds to 3-octyl acetate. **13C** (*tert*-butyl acetate) showed intense peaks at m/z 57 and 59. Characteristic peaks for the identification of 2-butyl acetate (**13D**) were m/z 87 and 101 corresponding to $[M^+ - C_2H_5]$ and $[M^+ - CH_3]$. 1,1-Dimethylpropyl acetate (**14C**) exhibited characteristic ions at m/z 101 and 115 due to $[M^+ - C_2H_5]$ and $[M^+ - CH_3]$. 1,2-Dimethylpropyl acetate (**14E**) was identified by direct comparison of its mass spectrum (Table XVII*) with that in the literature.[23]

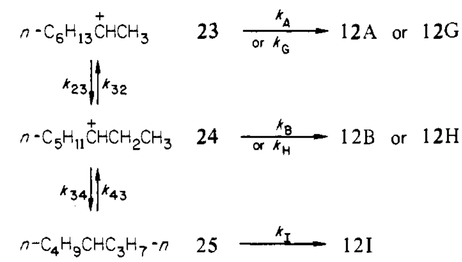
Compound **12I** was identified as 4-octyl acetate, based on the highly characteristic fragmentation pattern (β-cleavage to the ester bond); peaks due to $[M^+ - C_4H_9]$ at m/z 115 and to $[M^+ - C_3H_7]$ at m/z 129 are clearly seen; this is the same pattern as previously reported.[17]

Alkenes **12D**, **12E**, **13B**, and **14B** have already been discussed in the methanol solvolyses. Alkenes **10D**, **11E**, **11F**, and dimeric alkene **13F** gave spectra identical with literature data.[23] Propene **1D** showed peaks at m/z 42 (M^+) and 41 $[M^+ - 1]$. 1-Pentene (**11F**) and 2-pentene (**11E**) gave the molecular ion at m/z 70. The distinction between both isomers was done according to the intensity of m/z 42 (100) for **11F** and m/z 55 (100) for **11E**. 2,4,4-Trimethyl-1-pentene (**13F**) showed peaks at m/z 112 (M^+) and 57 $[(CH_3)_3C^+]$, 100. Products **13B**, **13C**, **13F**, **14B**, **14C**, and **14E** showed heavy deuterium incorporation (Tables XVII–XIX*).

Solvolyses in Acetic-d_3 Acid-d. The above conclusions were supported by results obtained for the solvolysis of **13** and **14** in CD_3CO_2D as solvent. Product **13D** showed a mass spectrum similar to that for solvolysis in CH_3CO_2H *except* that the following fragments (i.e., containing the CH_3CO group) all showed just d_3 peaks: $[CD_3C{\equiv}O]^{+\cdot}$, $[CD_3CO_2CHCH_3]^+$, and $[CD_3CO_2CHCH_2CH_3]^+$ at m/z 46, 90, and 104, respectively. Similarly, product **13E** gave d_3 peaks: $[CD_3C{\equiv}O]^+$, $[CD_3C(OH)_2]^+$, and $[CD_3CO_2CH_2]^+$ at m/z 46, 64, and 76, respectively.

However, products **13B** and **13F** showed extensive deuteration throughout and product **13C** extensive deuteration in the alkyl group as well as complete deuteration of the acetoxy group (Table XX*). The same pattern is repeated for the solvolysis products of **14**. **14B** shows extensive deuteration throughout, and **14C** and **14E** show complete deuteration of the acetoxy group as well as further extensive deuteration (Table XX*).

Scheme II. Rearrangements in Octyl System



Mechanistic Inferences from Nature of Solvolysis Products

The results of the product identifications and analyses are summarized in Table XXI. This shows products formed via olefin and not via olefin on the basis of the deuteration experiments, and the percent reaction to give normal substitution products, rearranged substitution products, and olefins. Substitution products are broken down into the number of rearrangements involved.

Unbranched Compounds. The experiments with deuterated solvents showed that neither the unrearranged nor the rearranged products from the solvolyses of **10**, **11**, and **12** in methanol and in acetic acid are formed via olefin intermediates. The rearranged products therefore arise by an S_N1-like reaction, i.e., either by path b or path c of Scheme I. In the case of the *n*-octyl derivative **12**, further rearrangement of the 2-octyl cation (**23**, *n*-C_6H_{13}) can occur to give the 3-octyl (**24**), and then the 4-octyl cation (**25**). Competition occurs between such further rearrangements and trapping of the octyl cations by solvent; the more nucleophilic solvent CH_3OH gives a greater 2-octyl:3-octyl ratio than AcOH as expected.

The proportion of rearranged to normal product is always higher for acetolysis, but as the chain length increases (**10** → **11** → **12**), it *decreases* for acetolysis, but *increases* for methanolysis.

Polyrearrangements are possible and are observed for the octyl derivative (**12**). Here **2** → **5** has a competing reaction as set out in Scheme II. For the acetolysis we assume

$$k_1 = k_H = k \neq k_G \quad (1)$$

$$k_{23} = k_{34} = k_{43} = k_{32} = k' \quad (2)$$

It is now possible to set up steady-state equations for **24** and **25**:

$$k'[\mathbf{23}] + k'[\mathbf{25}] = 2k'[\mathbf{24}] + k[\mathbf{24}] \quad (3)$$

$$k'[\mathbf{24}] = k'[\mathbf{25}] + k[\mathbf{25}] \quad (4)$$

and product ratio equations:

$$k[\mathbf{24}]/k_G[\mathbf{23}] = [\mathbf{12H}]/[\mathbf{12G}] = 0.16 \quad (5)$$

$$k[\mathbf{25}]/k[\mathbf{24}] = [\mathbf{12I}]/[\mathbf{12H}] = 0.5 \quad (6)$$

These equations can be solved to give $k' = k$ and $k_G = 2.4k$.

Branched Compounds. In CH_3OH, the deuteration experiments show that all the products are formed via olefin. Particularly in the case of **13**, it is likely that both $(CH_3)_2CHCH_2OCH_3$ and

Table XXII. Properties of Products Formed by *First* Step of Different Types in Solvolyses of Neopentyl and Isobutyl Derivatives

		neopentyl		isobutyl			
substituent	solvent	N substn	Me migrn	N substn	Me migrn	H migrn	elimination
Rpy^+	MeOH		100				100
Rpy^+	AcOH	15	85	21	20	59	
ROTs[a]	EtOH	8	92	95		5	
ROTs[a]	AcOH		100	21		79	
ROTs[a]	CF_3CO_2H		100		20	80	

[a] References 3 and 5.

Table XXIII. Individual Rates ($10^5k_{obsd}/s^{-1}$) for Formation of Unrearranged Substituted Products

reaction	temp, °C	Me	Et	*n*-Pr	*n*-Pent	*n*-Oct	*i*-Bu	*neo*-Pent
Rpy^+ + MeOH	150	1.9	11.0	8.6	8.6	4.3	<0.1[a]	<0.03[a]
Rpy^+ + AcOH	150	1.3	2.9	1.8	2.3	1.6	0.76	0.86
ROTs[b] + EtOH	75	6.9	2.9	1.94			0.12	0.0001
ROTs[b] + AcOH	75	0.085	0.077	0.061			0.0049	<0.0002[a]
ROTs[b] + CF_3CO_2H	75	0.0018	0.023	0.022			<11[a]	<0.2[a]

[a] Assume 2% of product would have been detected. [b] References 3 and 5.

Table XXIV. Individual Rates ($10^5k_{obsd}/s^{-1}$) for Products Formed by Proton- or Methyl-Migration Step

		H migration				Me migration	
reaction	temp, °C	*n*-Pr	*n*-Pent	*n*-Oct	*i*-Bu	*i*-Bu	*neo*-Pent
Rpy^+ + MeOH	150	0.02	0.09	0.52	<<5[a]	<0.1[b]	1.6
Rpy^+ + AcOH	150	0.24	0.28	0.44	<2[c]	0.73	4.8
ROTs[d] + EtOH	75	<0.04[b]			0.006	<0.003[b]	0.0016
ROTs[d] + AcOH	75	0.0001			0.018	<0.0005[b]	0.0083
ROTs[d] + CF_3CO_2H	75	0.15			4.4	1.1	11

[a] Corresponding product considered to be formed by an elimination mechanism. [b] Assume 2% of product would have been detected. [c] Part of product could be formed by an elimination reaction. [d] References 3 and 5.

Table XXV. Ratio of Migration to Direct Substitution

	H migration				Me migration	
reaction	*n*-Pr	*n*-Pent	*n*-Oct	*i*-Bu	*i*-Bu	*neo*-Pent
Rpy^+ + MeOH	0.002	0.01	0.1			>50
Rpy^+ + AcOH	0.1	0.1	0.3	<3	1	5
ROTs + EtOH	<0.02			0.05	<0.02	16
ROTs + AcOH	0.001			4	<0.1	42
ROTs + CF_3CO_2H	7			>0.4	>0.1	>55

$CH_3CH_2CHCH_3OCH_3$ would be stable under the reaction condition (cf. corresponding acetolysis products), and this suggests that all the products identified were produced via an initial elimination reaction, CH_3OH acting as base to give $(CH_3)_2C{=}CH_2$ which rapidly equilibrates with the solvent via $(CH_3)_3C^+$. Formation by path b or c (Scheme I) with methyl migration is less likely because if methyl migration occurs then hydrogen migration would presumably also occur (cf. acetolysis).

In AcOH, **13** clearly does not yield solely olefin derived products. Whereas the *t*-BuOAc and $(CH_3)_2C{=}CH_2$ products are completely deuterated (as the corresponding products from methanolysis), $(CH_3)_2CHCH_2OAc$ and $CH_3CH_2CH(OAc)CH_3$ are also produced and these contain no deuterium. The $(CH_3)_2CHCHOAc$ is clearly formed by *either* path a or path d of Scheme I. Formation of $CH_3CH_2CH(CH_3)OAc$ involves methyl migration *either* by path b or by path c; intermediate **2** is here a secondary carbenium ion. The olefin-derived products could involve *either* elimination *or* hydrogen migration by path b or c; this now leads through a tertiary carbenium ion which would equilibrate with olefin.

Elimination cannot occur as the *first* step for the neopentyl case; the initial step can be either direct substitution *or* methyl migration. The former is observed only in acetolysis, the latter is both methanolysis and acetolysis. Methyl migration leads to a tertiary carbenium ion which equilibrates rapidly with olefin.

We thus deduce that the proportions of the *first* step in the solvolyses of **13** and **14** are as in Table XXII; this table also contains similar data for tosylate solvolyses.[3,5]

Individual Rates of Formation of Unrearranged Substitution Products. Table XXIII gives the individual rates for the formation of these products, calculated from the total rate and the product composition. These products could arise by either (or both) of paths a and d of Scheme I. For the tosylates, the rate falls dramatically for the isobutyl and neopentyl compounds in both EtOH and AcOH (rate range ca. 10^5), and the same trend is found for the *N*-alkylacridiniums in MeOH. All this is consistent with the S_N2 path a of Scheme I. However, for the *N*-alkylacridiniums in AcOH, the rates are constant within a factor of $\sim$4; this cannot be reconciled with path a, but is just what is expected for the ionization of path d. For the tosylates in CF_3CO_2H no conclusion is possible as only limiting rates are available.

Individual Rates for the Formation of Products Arising by a H- or Me-Migration Step. Table XXIV gives the rates for these migrations, again calculated from the total rate and the product composition. This represents products formed by path b and/or path c of Scheme I (products deduced to be formed *in the initial step* by an elimination reaction have been omitted from consideration).

For the solvolysis of the *N*-alkylacridiniums in AcOH we have already implicated the intermediate ion-molecule pair (**4**) in the formation of the unrearranged products by path d. If path c, with the common intermediate **4**, operates for the formation of the rearranged products, the ratio of migration to direct substitution should be constant over the series for H migration and for Me migration. Table XXV shows that this is approximately so for the *N*-alkylacridinium salts in acetic acid.

By contrast, where the direct substitution occurs by path a, i.e., for the *N*-alkylacridiniums in MeOH and for the tosylates in EtOH and AcOH, such constancy of ratios are neither expected nor observed (Table XXV).

The above reasoning is a firm basis to assign path c to the formation of the rearranged products for the *N*-alkylacridiniums

Table XXVII. Activation Parameters for Primary Alkyl Derivatives

	acridiniums				tosylates					
	CH_3OH		CH_3CO_2H		EtOH		CH_3CO_2H		CF_3CO_2H	
substituent	$\Delta H^{\ddagger\,a}$	$\Delta S^{\ddagger\,a}$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
methyl			26.5	−19.1	17.8	−26.6[b]	22.6	−20.9[c]	22.0	−31.0[d]
ethyl	13.4	−45.9	28.1	−13.4	19.4	−23.8[b]	24.4	−16.7[c]	21.8	−26.7[d]
n-propyl	13.8	−45.4	29.0	−11.8	19.7	−20.4[e]	23.8	−18.8[f]	23.7	−17.2[d]
n-pentyl	9.2	−56.8	26.8	−16.9						
isobutyl	14.1	−45.5	33.0	−2.3	22.1	−22.1[b]	28.2	−8.0[c]	23.9	−9.7[d]
neopentyl	18.1	−38.7	32.8	−0.9	32.0	−2.4[b]	31.5	−1.0[g]	23.8	−8.9[d]

[a] $\Delta H^\ddagger$ in kcal mol^{-1}; $\Delta S^\ddagger$ in cal mol^{-1} K^{-1}. [b] Calculated from kinetic data in ref 2, 32, and 34. [c] From ref 2 and 34. [d] From ref 5. [e] Calculated from kinetic data in ref 32. [f] Calculated from kinetic data in ref 33. [g] Reference 8 also gives $\Delta H^\ddagger$ = 30.7, $\Delta S^\ddagger$ = −3.1.

in AcOH. We believe that path c probably also applies for these compounds in MeOH in view of the absence of anchimeric assistance found for the β-methoxyethyl (**17**) and β-phenylethyl (**16**) compounds. Presumably, the reason for this is the crowded transition state that is involved in the formation of bridged intermediates when the leaving group is the acridine (**7**).

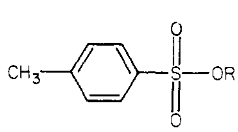
It is more difficult to draw conclusions regarding the mechanisms of formation of rearranged products by the tosylates; however, the similarity between the rate of H or Me migration in a tosylate in CF_3CO_2H (at 75 °C) with that for the corresponding alkylpyridinium in AcOH (at 150 °C) (Table XXIV) is striking, and could indicate a similar mechanism by path c.

General Discussion of Mechanistic Scheme. We believe that we have demonstrated a change in mechanism for the alkylpyridiniums between MeOH and AcOH solvents; it remains to consider the causes of this mechanistic changeover.

The solvent MeOH species appears to be a better nucleophile for conventional S_N2 path a reaction than AcOH, but possibly the inverse is the case for reactions via the ion–molecule pairs (**4**). In addition, the greater polarizability of AcOH should help in the formation of the ion-molecule pairs, in which charge has been concentrated from the conjugated pyridinium system onto the saturated carbocation.

Activation Parameters. Activation parameters, particularly entropy values, can give mechanistic information[5,26–28] if trends within a series of related compounds are considered. Polar substituent effects and steric effects which cause internal bond and angle deformations have been connected with $\Delta H^\ddagger$ and solvent and steric effects which restrict freedom to internal rotation in a molecule with $\Delta S^\ddagger$.[29–31]

Reaction rates, determined spectrophotometrically as previously described[13,14,19] at variable temperatures (Table XXVI*), allow calculation of the activation parameters summarized in Table XXVII for the solvolysis of 14-(primary alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c,h*]acridinium tetrafluoroborates (**8–11**, **13**, **14**) in methanol and acetic acid. Table XXVII also lists literature[2,5,8,32–34] activation parameters for the solvolysis of primary tosylates (**26**).



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Comparison of Activation Entropies with Dominant Mechanisms. The activation parameters are calculated from total rates, and thus refer to the dominant pathways, as previously deduced. For the primary alkyl acridiniums we find significant grouping of $\Delta S^\ddagger$ values (cal mol^{-1} K^{-1}) with the dominant pathways as follows: (i) path a (Et, *n*-Pr in MeOH), $\Delta S^\ddagger$ = -46; (ii) path d (Me, Et, *n*-Pr, *neo*-Pent in AcOH), $\Delta S^\ddagger$ = -12 to -19; (iii) path c (*i*-Bu, *neo*-Pent in AcOH), $\Delta S^\ddagger$ = -1; (iv) elimination path e (*i*-Bu, *neo*-Pent in MeOH), $\Delta S^\ddagger$ = -38 to -46.

This pattern is in agreement with expectation: the most negative $\Delta S^\ddagger$ is expected for paths a and e which are bimolecular in type and require precise alignment. The least negative $\Delta S^\ddagger$ is expected for path c where the unimolecular step (**1** → **4** or **4** → **2**) will be rate determining. Path d could possess an intermediate $\Delta S^\ddagger$ for unimolecular **1** → **4** and bimolecular **4** → **3** which could both be rate determining.

For solvolysis of primary tosylates, we find that in each solvent the $\Delta S^\ddagger$ value shows a change to less negative magnitude at a different place in the series: in EtOH between *i*-Bu and *neo*-Pent, in AcOH at *i*-Bu, and in CF_3CO_2H at *n*-Pr. These are just the places where migration becomes important, and $\Delta S^\ddagger$'s are hence associated with a change from path a to paths c/d.

Conclusions

We conclude that the relative rates of formation of products by direct substitution and of products formed by hydrogen or methyl migration from *N*-alkylacridiniums offer no evidence for participation in the rate-determining step. The data offer evidence for mechanistic change over for the direct substitution products from classical S_N2 substitution in MeOH to mainly nucleophilic attack on ion-molecule pairs in AcOH solvent.

These conclusions are in accord with our previous work on these systems: pyrolysis of the *N*-*n*-octyl and *N*-*n*-dodecyl acridinium trifluoromethanesulfonate analogues (**8–11**, **13**, **14**) gave olefins with an isomer distribution suggesting an E1 mechanism with a primary carbocation intermediate.[35] Solvolysis of these compounds in phenol and in benzoic acid[17] gave products also interpreted as being formed via primary carbocations which underwent partial rearrangement before being trapped.

How far these conclusions are applicable to tosylates remains to be seen. Shiner[11a] and Ando[10] have concluded that rate-enhancing anchimeric assistance by bridging is small in neopentyl solvolysis although the secondary isotope effects are significant.

Experimental Section

UV spectra of reactants and products were measured on a Perkin-Elmer 330 spectrophotometer. Rate measurements at fixed wavelength were obtained with a Pye-Unicam SP6-550 UV–visible spectrophotometer. Reaction vessels (sealed glass tubes of 28 cm × 13.5 mm diameter) were controlled to ±1 °C in hot-blocks (Statim Model PROP). ^1H NMR and ^{13}C NMR spectra were measured with Varian Model EM 360 L and Joel FX 100 spectrometers, respectively (Me_4Si as an internal standard).

Gas chromatography/mass spectral analysis utilized an AEI MS-30 mass spectrometer (using a Kratos DS-55 data system) interfaced to a Pye 104 gas chromatograph. The column packings employed were 10% DEGS-PS on 80/100 Supelcoport 3% SP-2100 on 100/120 Supelcoport,

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or 10% Carbowax 20M on 100/120 Supelcoport (5 or 6 ft × 4 mm) in glass columns, 30-mL/min helium as the carrier gas at flow rates and temperatures as specified (Tables VI and X).

General Procedure for the Preparation of 14-(Primary alkyl)-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium Tetrafluoroborates (8–17) (Table I). Method A. 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]-xanthylium tetrafluoroborate[18] (6) (4.48 g, 0.01 mol) and the corresponding amine (0.01 mol) were stirred in ethanol (20 mL) for 24 h at room temperature. The product was filtered and crystallized.

Method B. 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium tetrafluoroborate[18] (6) (4.48 g, 0.01 mol), the corresponding amine (0.01 mol), and triethylamine (1.01 g, 0.01 mol) were stirred in CH_2Cl_2 (30 mL) for 3 h at room temperature. AcOH (0.120 g, 0.002 mol) was added and the mixture was stirred for 48 h. After the solution was with washed water and 10% HCl, the organic layer was dried with $MgSO_4$. Addition of Et_2O gave the product (except for **11** and **12** where the petroleum ether was used). The product was purified by dissolving in CH_2Cl_2 and reprecipitating with Et_2O or petroleum ether. Compounds (Table I) were characterized by C, H, N analysis (Table XXVIII*), UV, NMR, and ^{13}C NMR (Table II*). **5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridine (7)** was prepared from 5,6,8,9-tetrahydro-7-phenylxanthylium tetrafluoroborate according to the literature method.[18]

Kinetic Measurements. Kinetics were followed by UV spectrophotometry monitoring the decrease of absorbance of the acridinium cation at fixed wavelength (386 nm) using the procedure already described.[19] In typical runs under pseudo-first-order conditions the concentration of acridinium compound was 6.4×10^{-5} M. A slightly different procedure was utilized for trifluoroacetic and acetic acids: the kinetic solutions of the acridinium compound (1.6×10^{-3} mol L^{-1}) were diluted to the UV concentration (6.4×10^{-5} mol L^{-1}) using a 4% (v/v) solution of triethylamine in ethanol before UV measurement (this converted acridine (7) into free base). Pseudo-first-order rate constants were calculated from the slope of conventional plots of ln $[(\epsilon_1 - \epsilon_2)/(\epsilon - \epsilon_2)]$ vs. time.[36] Such plots were linear to at least 80–90% completion, and k values were reproducible to ca. 5%.

Solvolysis Procedure by GC/MS Study. The acridinium compound (0.5 g) in 0.5 mL of solvent was heated in a sealed glass tube at 150 °C for 24–48 h. The tube was opened immediately before using for GC/MS study.

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Registry No. 6, 53217-56-4; **8**, 90886-02-5; **9**, 90886-03-6; **10**, 88125-57-9; **10A**, 557-17-5; **10B**, 109-60-4; **10C**, 108-21-4; **10D**, 115-07-1; **11**, 88125-58-0; **11A**, 628-80-8; **11B**, 6795-88-6; **11C**, 628-63-7; **11D**, 626-38-0; **11E**, 109-68-2; **11F**, 109-67-1; **12**, 90886-04-7; **12A**, 929-56-6; **12B**, 1541-09-9; **12C**, 54658-02-5; **12D**, 111-66-0; **12E**, 111-67-1; **12F**, 112-14-1; **12G**, 2051-50-5; **12H**, 4864-61-3; **12I**, 5921-87-9; **13**, 90886-05-8; **13A**, 625-44-5; **13B**, 115-11-7; **13C**, 540-88-5; **13D**, 105-46-4; **13E**, 110-19-0; **13F**, 107-39-1; **14**, 90886-07-0; **14A**, 994-05-8; **14B**, 513-35-9; **14C**, 625-16-1; **14D**, 926-41-0; **14E**, 5343-96-4; **15**, 81128-08-7; **16**, 82135-18-0; **17**, 90886-09-2.

Supplementary Material Available: Tables II (^{13}C NMR data for **8–17**), III (UV data for **7–17**), VIII, IX, XI–XX (mass spectral data for **10–14**), XXVI (solvolysis rate constants for **8–11**, **13**, **14**), and XXVII (analytical data for **8–17**) (16 pages). Ordering information is given on any current masthead page.

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Bis Heteroannulation. 4. Facile Syntheses of Methylene Acids, Methylbutenolides, α-Methyl-γ-lactones, and Related Materials. Total Syntheses of (±)-Ligularone and (±)-Petasalbine

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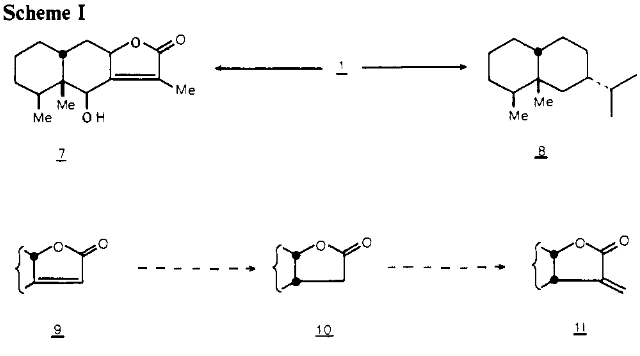
Abstract: Acetylenic oxazoles of proper design undergo an intramolecular Diels–Alder reaction leading directly to fused ring furan derivatives ("bis heteroannulation"). With 5-ethoxyoxazoles the corresponding 2-ethoxyfurans are obtained, and these latter materials are excellent precursors for methylene esters, methylene acids, methylbutenolides, α-methyl-γ-lactones, and β-methylfurans. In similar fashion, acetylenic oxazoles unsubstituted in the 2-position have been utilized for highly efficient syntheses of (±)-ligularone and (±)-petasalbine.

The structural diversity of the sesquiterpenes is renowned, and it is of little surprise that these materials have been a source of continuing fascination for synthetic chemists. With their myriad of skeletal types and their relatively large number of asymmetric centers, members of this class have served as an important testing ground for new synthetic methodology. Furthermore, many of these efforts have culminated in elegant total syntheses.[1]

Scheme I



Our own work in this area has focused on the observation that virtually all of these materials, regardless of their complexity, exhibit certain structural features in common (cf. Chart I).[2] That

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