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Collisionally-Activated Dissociation of *N*-Alkylpyridinium Cations to Pyridine and Alkyl Cations in the Gas Phase[1]

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Abstract: Many *N*-alkylpyridinium cations undergo collisionally activated dissociation in the gas phase to form pyridine and the corresponding carbocation. Appearance potentials (A.E.) for this dissociation pathway for a wide variety of pyridiniums Py^+-R were estimated quantitatively from the thresholds for fragment ion appearance in the collisionally activated dissociation of these laser-desorbed pyridinium cations. These A.E. were compared with the energy differences $[\Delta\Delta H_f = \Delta H_f(Py) + \Delta H_f(R^+) - \Delta H_f(Py^+R)]$ determined by AM1 semiempirical MO calculations. These A.E. were frequently equal or close to the calculated energy difference, in particular this was so for all cases when R^+ cannot rearrange to a more stable cation. Values considerably below that calculated were found for some cases when cation rearrangement can take place. The results are interpreted as involving Py···R^+ ion/molecule pair intermediates in which rearrangement of R^+ can occur before dissociation.

During the past 10 years, extensive investigations of nucleophilic substitution at saturated carbon in solution, utilizing charged pyridinium substrates and neutral pyridines as leaving groups, have considerably enhanced our understanding of these reactions. Evidence has been presented[3] that such reactions can occur by five distinct mechanisms (see Scheme I): (a) electron transfer followed by radical pair collapse; (b) classical S_N2 bimolecular substitution; (c) S_N2 via ion/molecule pairs; (d) S_N1 via ion/molecule pairs; and (e) classical S_N1 unimolecular dissociation.

There are major advantages in the use of a neutral leaving group such as pyridine over an anionic leaving group.[3] Unimolecular reaction of a neutral substrate dissociating into two ionic species involves charge creation in the transition state: such reactions therefore require media of high dielectric constant to proceed at a measurable rate. Unfortunately, the roles of such a medium as solvent and as nucleophile are not easily disentangled. Advantageously, substrates with neutral leaving groups can undergo unimolecular reactions in media of low dielectric constant. Furthermore, the reaction scheme is less complex in that the distinction in the Winstein[4] scheme between a solvent-separated ion pair and a free carbocation (caused by strong electrostatic attraction) disappears: for positively charged substrates, an intimate ion/molecule pair is the only distinct intermediate between the original substrate and a free carbocation.[3]

There has been considerable recent interest in gas-phase analogues of solvolysis reactions, and progress to 1982 has been reviewed by Morton,[5] including considerable evidence for ion/molecule complexes, which were apparently first proposed in 1978.[6] However, nearly all of this early work referred to oxygen (cf., e.g., ref 7) rather than nitrogen compounds, and none related to *N*-alkyl derivatives of nitrogen heteroaromatics. Although a study of halopyrazolium ions[8] showed dealkylation, it is likely that this was

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(1) Part 26 in the series *Kinetics and Mechanism of Nucleophilic Displacements with Heterocycles as Leaving Groups*. For part 25, see: Katritzky, A. R.; Lamba, D.; Spagna, R.; Vaciago, A.; Prewo, R.; Bieri, J. H.; Stezowski, J. J.; Musumarra, G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1391.

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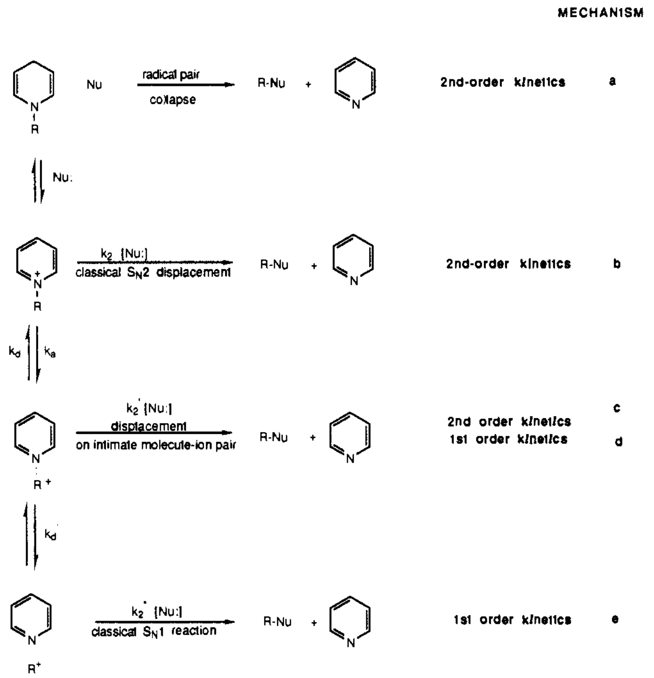
Table I. Preparation of the 1-Substituted Pyridinium Salts (**1**)

compd no.	1-substituent R	anion X	preparation method	time, h	temp, °C	solvent	crystallization solvent[a]	form[b]	yield, %	mp (°C) found	lit.	ref
1a	CH_3	I	A	2	22	CH_3NO_2	Me	prisms	96	117–117.5	117	27
1b	$CH_2{=}CHCH_2$	Br	A	1	22	CH_3NO_2	A-Et	plates	76	94–96[c]	92–94	28
1c	$CH_3OCH_2CH_2$	Br	A	48	22	neat	A-Et	plates	40	128–130	130	29
1d	p-$NO_2C_6H_4CH_2CH_2$	Br	A	12	22	neat	A-Et	prisms	53	183–185	180	30
1e	p-$NO_2C_6H_4CH_2$	Br	A	5	22	CH_3NO_2	A	needles	95	225	224–225	31
1f	$C_6H_5CH_2CH_2$	Br	A	24	90	neat	A-Et	m.cryst	62	123–125	126	30
1g	$C_6H_5CH_2$	Br	A	3	22	CH_3NO_2	A-Et	m.cryst	85	96–98	98–100	33
1h	1-adamantanyl	ClO_4	A	2	0	CH_3NO_2	A	plates	54	256–258	256–258	32
1i	p-$CH_3C_6H_4CH_2CH_2$	BF_4	B	96	115	pyridine	A	needles	73	122–124	*d, e*	
1j	p-$CH_3C_6H_4CH_2$	Br	A	2	22	neat	A-Et	prisms	95	136–137	123–124	31
1k	p-$CH_3OC_6H_4CH_2CH_2$	BF_4	B	96	115	pyridine	A	needles	50	148–148.5	*d, e*	
1l	p-$ClC_6H_4CH_2$	Cl	A	10	22	CH_3NO_2	A	prisms	57	158–159[c,e]	60	35
1m	p-$BrC_6H_4CH_2$	Br	A	2	22	CH_3NO_2	A	plates	95	206–207	198–200	34
1n	$C_6H_5SCH_2$	ClO_4	A	5	22	neat	A-Et	m.cryst	67	68–70	68–69	36
1o	$C_6H_5CH{=}CHCH_2$	ClO_4	A	4	22	CH_3NO_2	A	m.cryst	81	70–72	73–74	37
1p	p-$CH_3OC_6H_4CH_2$	ClO_4	B	1	100	pyridine	Ac-Et	needles	84	132	132	42
1q	p-$CH_3C_6H_4CHBr$	Br	f	1	−50	$CHCl_3$	A-Et	m.cryst	90	173–175	175–177	38
1r	1-benzotriazolyl CH_2	Cl	A	2	50	CH_3NO_2	A-Et	m.cryst	51	218–218.5	*d, e*	
1s	$(C_6H_5)_2CH$	Br	A	48	100	CH_3NO_2	A-Et	m.cryst	80	210–212	215–216	39
1t	$(C_6H_5)_3C$	BF_4	A	1	22	CH_2Cl_2	A	m.cryst	85	173–178	177–186	40

[a] Me, methanol; A, ethanol; Et, diethyl ether; Ac, acetone. [b] m.cryst, microcrystals. [c] Crystallized with H_2O. [d] New compounds. [e] Correct analysis in Experimental Section. [f] Prepared by method of ref 38.

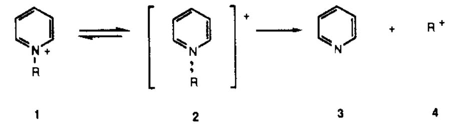
Scheme I. Nucleophilic Substitutions with Pyridines as Leaving Groups[a]



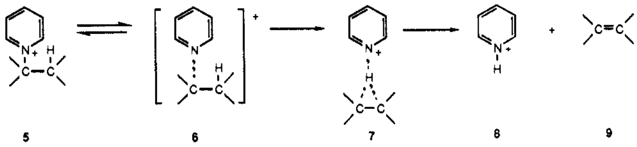
[a] Note Nu can be either neutral or negatively charged, and RNu is correspondingly positively charged or neutral.

a thermal reaction occurring during the desorption process. Diquaternary ammonium salts undergo dealkylation to give monocations by charge separation,[9] but here again the process may occur in the condensed phase. Clusters of type $NH_4^+\cdots NH_3$ have been studied, e.g., by Bowers and co-workers,[10] and evidence for the formation of complexes $R_3N\cdots R^+$ was presented in 1985 for both association[11] and dissociation[12] reactions. Bowen has extensively investigated[13] complexes of type $R^+\cdots NH{:}CHR'$, shown to be involved in the decomposition of imminium cations. In a recent paper he emphasized the importance of cation–neutral complexes and reported the unimolecular reactions of a variety of protonated aliphatic amines.[14] The gas-phase formation of ammonium ions by the process $R^+ + R'NH_2 \rightarrow RR'NH_2^+$ has also been observed.[11] However, none of this work provided quantitative energy values for dissociation energies, and it is in this respect that our paper is distinctive.

Scheme II. Fragmentation to Pyridine and Carbocation



Scheme III. Fragmentation to Pyridinium Cation and Alkene



The use of pulsed lasers to desorb involatile species has been quite successful in recent years,[15] particularly in conjunction with Fourier transform ion cyclotron resonance (FTICR) mass spectrometry.[16-20] The feasibility of desorbing and studying polymers,[21] biopolymers,[22] and a variety of other compounds[23-25] has

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been demonstrated. Initial success in our laboratories[24,25] with pyridinium ions suggested that this important class of charged species could be produced and studied in the gas phase by laser desorption (LD) FTICR mass spectrometry. We present in this and the following paper[26] the results of comparative studies of the collisionally activated dissociation of laser-desorbed *N*-alkylpyridinium cations, which has shed considerable light on their behavior. The present work also represents a natural extension of previous studies[12] on the infrared multiphoton and collisionally activated dissociation of gaseous alkylammonium ions.

Results and Discussion

Preparation of Compounds. The pyridinium salts investigated in this and the following paper were all prepared by one of two standard routes (see Experimental Section, Table I), method A from pyridine and the corresponding halide[27-40] or method B from the amine and a triphenylpyrylium cation,[41,42] to give the triphenylpyridinium salts which were reacted with pyridine.[43] All salts were characterized by ^1H and ^{13}C NMR spectroscopy (for details see ref 44).

Fragmentation Pathways. Two distinct pathways for collisionally activated dissociation were reported previously:[25] compounds (**1**) in which R is an adamantyl, phenylethyl, benzyl, *p*-methoxybenzyl, or trityl group, yielded pyridine (**3**) and the corresponding carbocation (**4**) (see Scheme II). The present paper concentrates on fragmentations of this type and describes a wide range of examples. Many compounds (**5**) which by β-elimination can yield a strain-free olefin (**9**) choose to form this olefin together with the pyridinium cation (**8**) (see Scheme III): this type of fragmentation is treated in the following paper.[26]

There is considerable previous evidence that alkylammonium cations undergo gas-phase unimolecular fragmentation via loose complexes,[11,13,14] and we believe that such complexes (**2** and **6**) are involved in both Scheme II and Scheme III. These complexes correspond to the ion/molecule pairs for which much evidence has been obtained in solution.[3]

Appearance Energies from Low-Energy Collisional Activation. The use of collisional activation to obtain estimates for thermochemical quantities, as applied in this work, has been reported for several different mass spectrometric techniques. Early ion beam/collision chamber experiments[45] derived quite good bond strengths and electron affinities for relatively small negative ions from the onsets of endothermic reactions driven by excess ion kinetic energy. More recently, the same approach has been applied extensively to metal ions by using a guided beam apparatus.[46,47] One quantitative CAD application in a FTICR mass spectrometer, quite similar in concept to the work carried out here, has also been reported.[48] Gas-phase acidity estimates for large organic anions, of comparable size to the *N*-alkylpyridinium cations studied in our research, have also been obtained from CAD experiments in a flowing afterglow-triple quadrupole instrument.[49]

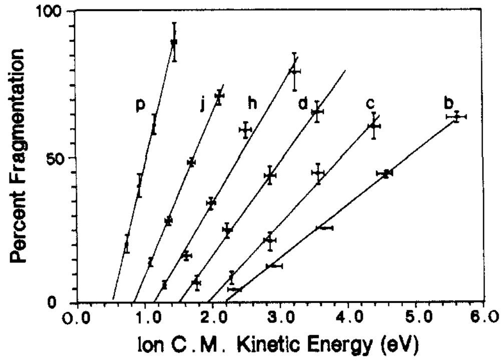

Figure 1. Percent of fragmentation of Py^+R to R^+ and Py versus nominal ion center of mass energy for some 1-substituted pyridinium cations (**1**): (**b**) allyl; (**c**) methoxyethyl; (**d**) (*p*-nitrophenyl)ethyl; (**h**) adamantyl; (**j**) *p*-methylbenzyl; (**p**) *p*-methoxybenzyl.

Uncertainties in thermochemical quantities derived from low-energy CAD experiments have been estimated to lie in the range 0.05–0.2 eV. Where detailed fitting of fragment ion appearance curves in the region above the threshold can be carried out (usually for relatively small ions), quite low error estimates have been given (0.05[45] and 0.1 ev[46]). An uncertainty of ±0.15 eV was estimated for the threshold center-of-mass energy in the triple-quadrupole experiments,[49] which apparently led directly to ±3.5 kcal/mol uncertainties in gas-phase acidities. The earlier FTICR study[48] estimated errors of 0.2 eV in the determination of threshold energies for endothermic processes. We consider in detail below a number of factors which affect the quality of the data produced by our CAD experiments involving *N*-alkylpyridinium ions, in order to obtain a justifiable and conservative estimate of the errors associated with these data.

The Ion Excitation Process. Calculation of the translational energy imparted to an ion during the excitation stage of the FTICR CAD process has most often[48,50] used the infinite parallel plate capacitor approximation given in eq 1

$$E_{\text{ion}} = q^2V^2t^2/8md^2 \tag{1}$$

where q is the ionic charge, V (1–7 $V_{\text{p-p}}$ in these experiments) is the amplitude of the RF excitation pulse,[51] t (1×10^{-4} s) is the RF pulse width, m is the ionic mass, and d (0.0254 m) is the distance between the excitation plates of the analyzer cell. However, since the actual FTICR cell in many cases is a cubic or rectangular box, electric fields and translational energies less than those calculated for an infinite parallel plate capacitor might be expected. Recent calculations and ion motion simulations[52] have shown that, in fact, ions near the center of a cubic cell (such as that used in these experiments) are excited to a radius only 0.72 of that predicted for an infinite parallel plate capacitor. Since an ion's translational energy is proportional to the square of its

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radius, actual excitation is only 0.52 of that predicted by eq 1. This correction has been made to all ion kinetic energies reported in this paper.[53]

While collisions after ion excitation are central to the CAD process, it is desirable that ions suffer no collisions *during* translational excitation. Otherwise, uncertainties in the amount of energy actually imparted during the excitation process will result. It is thus important to keep the excitation time as short as possible. In this work, an excitation time of 100 μs was used. At overall pressures of ca. 1×10^{-5} Torr, one can calculate an *average* time between ion/molecule collisions of 3.6 ms (assuming a Langevin[54] rate constant of 1×10^{-9} cc/s and a temperature of 350 K). Thus the average number of collisions in 100 μs is 1/36. It is apparent that during the 100 μs excitation time most ions will undergo no collisions; however, some will undergo one and very few two or more. The fraction of ions undergoing various numbers of collisions has been shown[55] to obey a Poisson distribution given by eq 2, where $\bar{n}$ is the average number of collisions in a given time period and n is the actual number of collisions.

$$P(n) = (\bar{n})^n \exp(-\bar{n})/n! \qquad (2)$$

By using eq 2 one can calculate that under the excitation conditions used in this work over 97% of the ions underwent no collisions in the excitation period, less than 3% suffered one collision, and a negligible number suffered two or more collisions.

The CAD Process. Following translational excitation, ions were allowed to collide with Ar neutrals during a 50-ms collision period. Above certain threshold levels of excitation, fragmentation to give R^+ and pyridine was observed. Extraction of the threshold energy for dissociation has been carried out according to the treatment of Chantry,[56] which takes into account the spread in both ion and neutral translational energies.

Plots of the percentage of fragmentation ($[R^+]/([Py^+R] + [R^+]) \times 100$) vs nominal ion center-of-mass (CM) energy (assuming stationary neutrals) were made, and the straight line portions of these plots were extrapolated to zero fragmentation. Typical plots are shown in Figure 1.

The true threshold energy, E_T, was obtained from the observed threshold, E_{obs}, by using eq 3[56]

$$E_T = E_{obs} + 0.6W_{1/2}(E_T) \qquad (3)$$

where $W_{1/2}(E_T)$ is given by eq 4[56]

$$W_{1/2}(E_T) = (11.1\gamma k T_b E_T)^{1/2} \qquad (4)$$

in which γ is the ion mass (m) divided by the sum of the ion and neutral masses ($m + M$), k is the Boltzmann constant, and T_b is the gas temperature, corrected for the spread in ion energies as discussed below.

Application of eq 3 above assumes that the cross section for fragmentation has a step-function behavior at energies above E_T. While this is almost certainly not the case, nothing is known about the actual form of the cross section above the threshold for ions as complicated as those dealt with here. Given the wide range of cross sections which have been used successfully[46] to fit even much simpler systems, the computationally straightforward approach discussed above, which has already been applied to larger ions,[49] was used to obtain threshold energies for fragmentation in this work.

Before ions are excited translationally in an FTICR cell, their original kinetic energy distribution is that of the neutral molecules from which they are formed (by electron impact) or by which they are "thermalized" following laser desorption (as in these experiments). However, this distribution is *not* maintained during the excitation process but becomes broader.[57] The spread in ion kinetic energies, ΔT, is given by eq 5

$$\Delta T = (E_{ion})^{1/2}\epsilon^{1/2} + \epsilon \qquad (5)$$

where E_{ion} is given by eq 1 (multiplied by the factor of 0.52 discussed above), and ϵ is a measure of the spread in thermal energies. Although not discussed in ref 57, this spread should apply only to thermal energies in two dimensions—those defining the plane in which the ions are excited. Their motion in the third dimension (along the magnetic field direction) is not (at least to first order) coupled to excitation in the plane perpendicular to the magnetic field. The two-dimensional energy spread of the ions prior to excitation was taken to be (full-width at half maximum of the 2-D Boltzmann distribution function) 1.5 kT,[56] which is 0.0543 eV at 350 K. This value was used in eq 5 to calculate the spread in ion energy after excitation. Multiplying by $M/(m + M)$ gave the spread in CM energy for a given ion translational energy.

A weighted linear least-squares program[58] which accounted for errors in both E_{CM} and the percentage of fragmentation was used to determine observed threshold values for fragmentation, E_{obs}. Errors in E_{CM} were obtained as discussed above, and errors in the percentage of fragmentation were calculated by standard statistical methods of estimation[59] for the replicate fragmentation experiments carried out at each collision energy. After E_{obs} (and its error estimate) were determined, an initial guess was made as to E_T. The spread in ion CM energy for E_T was then calculated by using eq 5. This spread was used in eq 6[56] to calculate the effective temperature of the neutrals, T_b, taking into account the spread in ion energies

$$kT_b = kT + \left(W^2_{1/2,b}/11.1\gamma E_T\right) \qquad (6)$$

where T is the temperature of the neutral gas (taken as 350 K in these experiments), $W_{1/2,b}$ is the spread in ion CM energy, and γ is as defined in eq 4. Equations 3 and 4 were then used to calculate a value for E_T from E_{obs}. This new value for E_T was used in place of the original guess, and the above process was repeated until a consistent value of E_T was obtained.

During a collision time of 50 ms, multiple collisions between translationally excited ions and the argon neutrals are certainly possible. However, given that ions are no longer being excited by this time, the *maximum amount of energy* available for conversion to internal energy of the ion is the CM energy corresponding to the initial translational excitation of the ion. Multiple collisions cannot impart any more energy than this and will probably be less efficient, as some of the relative translational energy can be carried off by the Ar neutral. Thus the threshold energy for fragmentation corresponds to those (admittedly unlikely) collisions in which all of the relative kinetic energy is converted in the ion/molecule collision complex into internal energy in the ion. With time, there is a finite probability that this internal energy will be localized in the normal mode which corresponds to cleavage of the weakest (N–R) bond in these *N*-alkylpyridinium compounds. Since little reverse activation energy is expected for such simple bond cleavage reactions, the appearance energy for fragmentation should provide a good estimate of the bond strength. (This is not the case for olefin formation—see following paper.)

The problem of "kinetic shifts", in which slow fragmentations are not observed due to the short time scale for ion detection in some mass spectrometers, is minimized in FTICR experiments. Since there is a delay of many milliseconds between the activating ion/Ar collisions and detection of parent and fragment ions, all but extremely slow fragmentations (with lifetimes of milliseconds, rather than the usual microsecond or shorter lifetimes for dissociation) will be observed.

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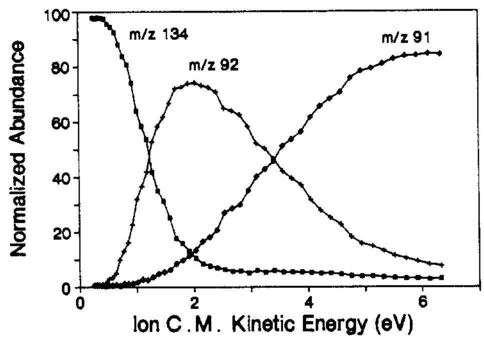

Figure 2. Breakdown diagram for *n*-butylbenzene parent ions resulting from low-energy CAD.

Table II. Results of Calibration Experiments

compd	fragmentation process	threshold,[a] eV	lit. eV	difference, eV
n-butylbenzene	m/z 134 → m/z 92	1.09	0.99[b]	0.10
	m/z 134 → m/z 91	1.98	1.61[b]	0.37
nitrobenzene	m/z 123 → m/z 93	0.82	1.20[c]	−0.38
	m/z 123 → m/z 77	1.65	1.27[c]	0.38

[a] Determined by using the procedures described in the text, including the internal energy correction from 350 to 0 K. [b] Reference 60. [c] Reference 61.

Calibration Experiments. To check the validity of these CAD experiments in obtaining estimates of N–R bond strengths, comparison of our experimental results with previously determined values would be desirable. This approach proved quite successful in earlier studies of large carboxylate anions.[49] However, to our knowledge, no reliable thermochemical values are available. We thus chose two well-studied ionic systems of similar complexity to those under investigation here, *n*-butylbenzene[60] and nitrobenzene.[61] Figure 2 shows the breakdown curves obtained for *n*-butylbenzene parent and fragment ions. By using the methodology detailed above, the threshold energies for two different fragmentations in each of these two systems were determined. The results are summarized in Table II.

Threshold energies determined in this work correspond to the process in which ions with internal energies corresponding to a nominal temperature of 350 K dissociate with just enough energy to form a fragment ion and neutral with no kinetic energy and with internal energies corresponding to 0 K. Thus to compare with earlier results,[60,61] which had been converted to 0 K values for both the parent ion and fragmentation products, a correction[60] of $^3/_2kT$ for rotational energy and $h\nu/[\exp(h\nu/kT) - 1]$ for each normal mode was added to our results to obtain the 0 K results. Frequencies used for *n*-butylbenzene and nitrobenzene ions were those given or estimated in the comparison experiments.[60,61] An average internal energy of 0.31 eV for *n*-butylbenzene and 0.20 eV for nitrobenzene were obtained for 350 K ions.

Given the agreement shown in Table II between our CAD experiments and the earlier work, an uncertainty of 0.35 eV (8 kcal mol) seems quite reasonable, and this conservative estimate has been applied to all experimentally derived appearance energies given in this paper.[62]

A related, but slightly different, approach was taken to correct for internal energies in the *N*-alkylpyridinium results given in Table III. In this case, the energies of the pyridine neutral and R^+ fragment were corrected from 0 K to 350 K. Reported[63] frequencies for pyridine were used to calculate an average internal energy of 0.12 eV at 350 K. Average internal energies for the R^+ ions at 350 K were either calculated by using vibrational frequencies for neutrals of similar structure (e.g., p-$BrC_6H_4NO_2$[64] for p-$BrC_6H_4CH_2^+$) or estimated/interpolated from the values calculated for *n*-butylbenzene, nitrobenzene, p-$BrC_6H_4CH_2^+$, and pyridine. The average R^+ internal energy (350 K) estimated in this way and our determination of the energy required for the process

$$N\text{-alkylpyridine}^+ \text{ (350 K)} \rightarrow R^+ \text{ (350 K)} + \text{pyridine (350 K)}$$

are given in Table III. Internal energies were corrected to 350 K rather than 0 K primarily to facilitate comparison with AM1 calculations (vide infra), which are parameterized with 298 K heats of formation. Any errors due to the fact that calculations are referred to 298 K and experimental results are corrected to 350 K should be small compared to our uncertainties.

Appearance energies for the process $Py^+R \rightarrow Py + R^+$ for 18 alkyl-substituted pyridines, determined in the manner discussed above, are given in Table III. Among the ions which dissociate to pyridine and a carbocation by the pathway of Scheme II, the stability order is quite significant, with wide variation in the appearance potentials. We consider later the effect of para substituents in the benzyl and β-phenylethyl derivatives and first discuss the effect on the appearance potentials of substituents in 1-methylpyridinium cations.

Effect of Substituents in the Methyl Group on the Dissociation of 1-Methylpyridinium Cation. The parent compound is very stable, and its appearance potential is outside our measurement range i.e., >93 kcal/mol. The appearance potential is lowered if the R^+ positive charge can be delocalized over a conjugative carbon skeleton: 67 kcal/mol for allyl (**1b**), 45 kcal/mol for benzyl (**1g**), 30 kcal/mol for cinnamyl (**1o**), and 24 kcal/mol for diphenylmethyl (**1s**). For trityl (**1t**), it is below 9 kcal/mol, our lowest observed A.E. measurement limit.

If the positive charge can be delocalized onto a heteroatom, the appearance potential is also considerably depressed: 64 kcal/mol for methoxymethyl (**1c**), 32 kcal/mol for (phenylthio)methyl (**1n**), and 24 kcal/mol for benzotriazolylmethyl (**1r**). The effect of a large saturated carbon skeleton is also very significant, the 1-adamantyl (**1h**) A.E. being 43 kcal/mol. The series β-phenylethyl (**1f**) 49 kcal/mol, benzyl (**1g**) 45 kcal/mol, cinnamyl (**1o**) 30 kcal/mol, and diphenylmethyl (**1s**) 24 kcal/mol shows successively decreasing A.E. values; as is discussed later, in all these cases an exothermic rearrangement occurs which helps to lower these A.E. values.

Effect of Para Substituents on the Dissociation Energy of 1-(Para-substituted Benzyl)- and 1-(Para-substituted β-phenylethyl)pyridinium Cations. As expected, within each series, electron donor substituents lower the appearance potentials, and electron-withdrawing substituents raise the appearance energy. It is remarkable that all the β-phenylethyl compounds decompose exclusively to R^+ and Py and give no styrene ($ArCH{=}CH_2$) and PyH^+. This point is discussed further in the following paper.[26]

Calculations. Since reliable thermochemical data are not available for comparison with experimentally derived appearance energies, a theoretically calculated energy of pyridine$^+$–R bond cleavage was used instead. Heats of formation were thus calculated for the pyridinium ions Py^+R, for pyridine, and for the alkyl cations R^+ by using the AM1 method.[66] From these ΔH_f values the theoretical heats of dissociation $\Delta\Delta H_f$ for the process of Scheme II were calculated with eq 7. These theoretical results are listed in Table III.

$$\Delta\Delta H_f = [\Delta H_f(\text{Py}) + \Delta H_f(\text{R}^+)] - \Delta H_f(\text{Py}^+\text{R}) \qquad (7)$$

Assessment of Accuracy of Calculations. Dewar et al.[66] calculated the heats of formation for a wide variety of compounds via the AM1 method. An average error of 5.3 kcal/mol was found for 58 different hydrocarbons. The average error for 80 com-

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Table III. Fragmentation of 1-Substituted Pyridinium Cations

compd no.	1-substituent R	appearance energy of R^+,[a] kcal/mol	R^+ internal energy (350 K),[b] kcal/mol	corrected appearance energy (350 K),[c] kcal/mol	ΔH_f, kcal/mol				$\Delta\Delta H_f$,[d] kcal/mol		
					Py^+R	R^+	tropylium	spiro	R^+	tropylium	spiro
1a	CH_3	>93		>96	186	252			98		
1b	$CH_2{=}CHCH_2$	61	3	67	204	223		261[e]	51		89
1c	$CH_3OCH_2CH_2$	57	4	64	138	178		180[e]	72		74
1d	p-$NO_2C_6H_4CH_2CH_2$	46	7	56	220	256	223	258	68	35	70
1e	p-$NO_2C_6H_4CH_2$	43	6	51	227	244	234		49	39	
1f	$C_6H_5CH_2CH_2$	40	6	49	210	242	201	236	64	23	58
1g	$C_6H_5CH_2$	38	5	45	214	223	212		41	30	
1h	1-adamantyl	36	4	43	155	169			46		
1i	p-$CH_3C_6H_4CH_2CH_2$	27	7	37	201	233	192	224	64	23	55
1j	p-$CH_3C_6H_4CH_2$	27	6	36	206	211	201		37	27	
1k	p-$CH_3OC_6H_4CH_2CH_2$	25	8	36	171	202	159	187	63	20	48
1l	p-$ClC_6H_4CH_2$[f]	26	5	34	209	217	208		40	31	
1m	p-$BrC_6H_4CH_2$	23	6	32	222	231	222		41	32	
1n	$C_6H_5SCH_2$	23	6	32	229	288	219	254	91	22	57
1o	$C_6H_5CH{=}CHCH_2$	21	6	30	229	225	225		28	28	
1p	p-$CH_3OC_6H_4CH_2$	19	7	29	175	174	168		31	25	
1q	p-$CH_3C_6H_4CHBr$	18	6	27	219	216	212		29	25	
1r	1-benzotriazolyl-CH_2	16	5	24	312	307	251		27		
1s	$(C_6H_5)_2CH$	15	6	24	246	234	232		20	18	
1t	$(C_6H_5)_3C$	<9			290	258			0		

[a] Corrected for energy spread in ions and neutrals, as discussed in text. [b] Calculated or estimated as described in text. [c] For the process Py-R (350 K) → Py (350 K) + R^+ (350 K). Internal energy of Py (350 K) = 0.12 eV (3 kcal/mol) has been added to the sum of the previous two columns. [d] See eq 7, $\Delta H_f(Py)$ = 32.1 kcal/mol.[65] [e] Calculated for the cyclic structure of cation (see text). [f] m/z 169 [$Py^+CH_2C_6H_4Cl \rightarrow Py^+CH_2C_6H_4$] is formed in 16% of abundance.

Table IV. Comparison of Theoretical (AM1) and Experimental ΔH_f Values[a]

	AM1	exptl[b]	Δ[c]
	Ions		
CH_3^+	252	261	-9
$C_2H_5^+$	217	216	1
$C_3H_5^+$	223	226	-3
n-$C_3H_7^+$	208	211	-3
i-$C_3H_7^+$	192	191	1
n-$C_4H_9^+$	200	203	-3
sec-$C_4H_9^+$	184	183	1
i-$C_4H_9^+$	202	199	3
t-$C_4H_9^+$	174	166	8
$C_5H_9^+$	186	191	-5
$C_5H_6N^+$	184	178	6
$C_6H_5CH_2^+$(benzyl)	223	215	8
$C_7H_7^+$ (tropylium)	212	203	9
$C_6H_5CH^+CH_3$	207	199	8
	Neutrals		
C_2H_4	16.5	12.5	4
C_3H_6	6.6	4.8	2
1-C_4H_8	0.4	-0.1	0.5
2-C_4H_8	-2.3	-1.9	-0.4
i-C_4H_8	-0.7	-4.0	3.3
cyclopropyl=CH_2	48	48	0
c-C_5H_8	3.0	8.6	-5.6
cyclobutyl=CH_2	25.1	29.6	-4
2-C_5H_{10}	-9	-6.3	-3
C_5H_5N	32	33	-1
$C_6H_5CH{=}CH_2$	39	35	4

[a] All values in kcal/mol. [b] From ref 67. [c] Δ = ΔH_f(calc) − ΔH_f(exp).

pounds containing nitrogen and/or oxygen was 5.8 kcal/mol. A slightly lower average error of 4.7 kcal/mol was found for 15 cations.

Table IV lists ΔH_f values (AM1 calculations and experimental) for 14 ions and 11 neutrals whose heats of formation have been calculated for use in appearance energy comparisons in this and the following paper and for which reasonably reliable experimental values are also available.[67] The heats of formation calculated by using the AM1 method are in good agreement with the experimentally determined values, with an average deviation between theory and experiment of 3.8 kcal/mol. No systematic errors can be observed for the calculated values. Assuming the experimentally determined values are correct, an uncertainty of ±5 kcal/mol seems reasonable for ΔH_f of ions calculated in this work.

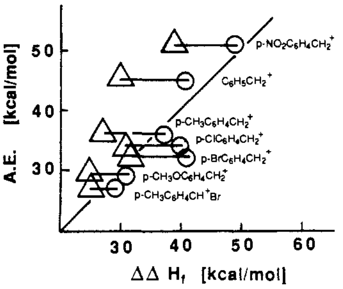

Figure 3. Plot of experimentally estimated appearance energies (A.E.) against calculated heats of formation ($\Delta\Delta H_f$) of R^+ from 1-(para-substituted benzyl)pyridinium salts: unrearranged benzyl cations (○); tropylium cations (△); data from Table III.

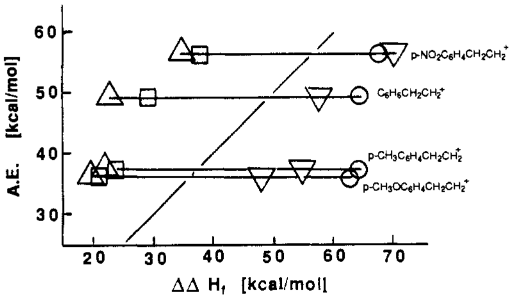

Figure 4. Plot of experimentally estimated appearance energies (A.E.) against calculated heats of formation ($\Delta\Delta H_f$) of R^+ from 1-(para-substituted phenylethyl)pyridinium salts: unrearranged β-phenylethyl cation (○); substituted tropylium cation (△); cations of spiro structure (▽); α-phenylethyl cations (□); data from Table III.

Given that the uncertainty in the appearance energies was estimated above to be ca. 8 kcal/mol, an average error of ca. 5 kcal/mol in the AM1 calculations is quite acceptable. We believe that the AM1 method provides good estimates of the heats of formation for ions where experimentally determined values are not available.

Experimental–Theoretical Comparison. The experimentally determined appearance potentials are plotted against theoretically calculated $\Delta\Delta H_f$ values in Figures 3–5 (open circles). It is evident that in many cases the appearance potentials occur at lower values than would be expected even for a dissociation process without

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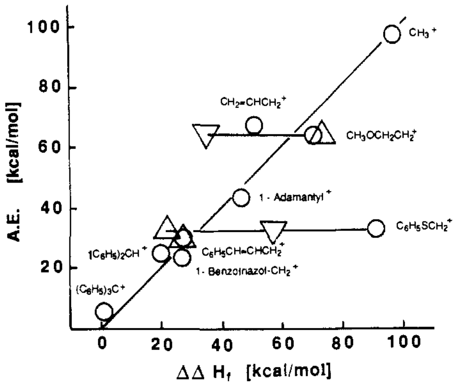
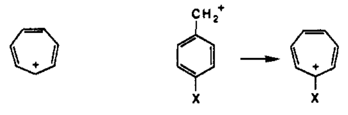


Figure 5. Plot of experimentally estimated appearance energies (A.E.) against calculated heats of formation ($\Delta\Delta H_f$) of R$^+$ from 1-substituted pyridinium salts: unrearranged cations (○); cations with successively more extensive rearrangement (▵, ▿, □); data from Table III; see text.

any energy of activation. This indicates that there is some other factor which reduces the energy required for the N–C bond cleavage reactions. Ions could have excess internal energy, but, after the 1s delay, IR radiation and collisions should have removed most of this excess energy. The most likely remaining explanation is reorganization of the structure of the positive carbonium ion R$^+$. We discuss the possibilities of such reorganization in three sets of ions—benzyl, β-phenylethyl, and others.

Formation of Benzyl Cations. The structures and energetics of gaseous $C_7H_7^+$ ions have been extensively investigated, both experimentally and theoretically. General experimental evidence, including the determination of appearance potentials and heats of formation,[68-70] supports the idea that these cations exist in the gas phase with at least two structures, benzyl and tropylium (**10**).[68,71,72] Benzyl cations are known to rearrange in the gas phase and in matrices to tropylium cations,[72,73-77] and substituted benzyl cations (**11**) rearrange to substituted tropylium cations (**12**).[73,75]



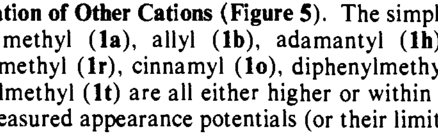
10 11 12

Experimental evidence has also been presented that one $C_7H_7^+$ isomer is reactive (benzyl) and the other unreactive (tropylium).[71,74,75,78,79] Other $C_7H_7^+$ isomers are possible, and McLafferty et al.[80,81] postulated that tolyl and norbornadienyl may exist as stable structures, but later studies have provided evidence for only the benzyl and tropylium cations.[72,77] Heats of formation for $C_7H_7^+$ have been calculated for the benzyl (ΔH_f = 217.1, 220.4 kcal/mol) and tropylium (ΔH_f = 207.9, 195.6 kcal/mol) structures.[82,83] Lias et al.[67] reported heats of formation for the benzyl and tropylium structures of 215 and 203 kcal/mol, respectively. The activation energy for conversion of benzyl to tropylium has been calculated to be 32.7 kcal/mol.[83]

We therefore calculated, by using the AM1 method, ΔH_f values for the tropylium isomers of the benzyl cations formed from (**1e**), (**1g**), (**1j**), (**1l**), (**1m**), and (**1p**) and thus determined modified $\Delta\Delta H_f$ values for the dissociation of Py$^+$CH$_2$Ar into pyridine and a (substituted)tropylium cation (see Table III).

Figure 3 shows the A.E. values plotted against $\Delta\Delta H_f$ values for formation of both the benzyl and the corresponding tropylium cation. For the parent benzyl compound (**1g**) and for the *p*-nitro- (**1e**), *p*-methyl- (**1j**), *p*-methoxy- (**1p**), and α-bromobenzyl (**1q**) derivatives, the experimentally determined appearance potentials are close (+4, +2, −1, −2, and −2 kcal/mol difference) to the AM1 calculated dissociation energies, indicating dissociation to the benzyl rather than tropylium cations. To verify this assignment, $C_7H_7^+$ ions formed by CAD from the parent benzyl compound (**1g**) were allowed to react with toluene. An ion–molecule reaction forming $C_7H_8^+$ was observed, indicating[71,75] a benzyl rather than tropylium structure for the $C_7H_7^+$ ion. However, for the corresponding *p*-chloro- (**1l**) and *p*-bromobenzyl (**1m**) compounds, the A.E. are lower than the calculated energies by 6 and 9 kcal/mol, respectively, which suggests that in these two cases some stabilizing factor occurs during the dissociation. The calculations indicate that rearrangement of the benzyl to the corresponding tropylium cation at the ion–molecule stage would provide enough energy to explain the lower A.E. observed for (**1l**) and (**1m**).

Formation of β-Phenylethyl Cations. Anchimeric assistance in the solvolysis of β-phenylethyl compounds, with the formation of spirocations of type **14** from **13**, is well established.[84-86] Comparison of the calculated $\Delta\Delta H_f$ values with the appearance potentials (Figure 4) indicates that not only is dissociation to unrearranged β-phenylethyl cations precluded but also that rearrangements of **13** to spiro **14** during the dissociation process do not provide enough stabilization energy. The low appearance potentials suggest either that further rearrangement of **14** to **16** must occur to a significant extent during the dissociation or that alternative rearrangement of **13** → **15** occurs. Calculations show ΔH_f of **15** to be 207, 191, 159, and 226 kcal/mol for X = H, CH$_3$, OMe, and NO$_2$, respectively.



14 13 15 16

The energies of **13**, **14**, **15**, and **16** have been discussed by McLoughlin et al.[68] For $[C_8H_9]^+$ the mean heat of formation was deduced from photoionization measurements to be 199.2 kcal/mol, which was interpreted as evidence of structure **15** and/or **16**. Our results are in good agreement with this.

Formation of Other Cations (Figure 5). The simple $\Delta\Delta H_f$ for R$^+$ for methyl (**1a**), allyl (**1b**), adamantyl (**1h**), 1-benzotriazolylmethyl (**1r**), cinnamyl (**1o**), diphenylmethyl (**1s**), and triphenylmethyl (**1t**) are all either higher or within 3 kcal/mol of the measured appearance potentials (or their limiting values) and indicate a moderate activation barrier (ca. 13 kcal/mol) for the formation of allyl.

The low appearance potential found for (phenylthio)methyl (**1n**) indicates that rearrangement of **17** occurs, through **18**, almost all the way to **19**, with this $\Delta\Delta H_f$ of 22 kcal/mol closest to the appearance potential of 32 kcal/mol.

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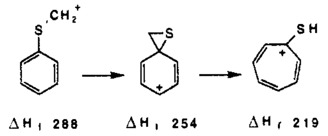


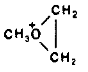
17 18 19

For the 2-methoxymethyl compound (**1c**), anchimeric assistance by the proton migrating toward structure **20** may be indicated, although the A.E. (67 kcal/mol) is quite close to $\Delta\Delta H_f$ for $CH_3OCH_2CH_2^+$ of 73 kcal/mol (the spiro compound (**21**) is of higher energy).

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

ΔH f 141

20



ΔH f 180

21

Conclusions

Overall, there is excellent agreement between the calculated $\Delta\Delta H_f$ values, and the experimentally derived A.E. provided allowance is made for carbonium ion rearrangement. A satisfactory interpretation of the dissociation processes of pyridinium cations in the gas phase invokes the $Py\cdots R^+$ ion–molecule pair as an important intermediate in which nonstabilized R^+ can rearrange to a more stable structure. The possibility of rearrangement to Py^+H and an olefin is discussed in the following paper.[26]

Experimental Section

All mass spectrometric studies were carried out in a Nicolet FT MS-1000 Fourier transform ion cyclotron mass spectrometer equipped with a 3 T superconducting magnet. The important features of this technique have been described elsewhere.[16–20] The mass spectrometer was operated in a broad band mode, which encompasses a mass range of 17–3000 daltons. Ions were detected by the standard frequency-chirp excitation method. Because of the high ionization efficiency of laser desorption, 3–5 ion formation/detection cycles were sufficient to obtain a spectrum with an acceptable signal-to-noise ratio. For each spectrum 16384 data points were acquired, and this data set was zero-filled once before performing the Fourier transform.

Collisionally activated dissociation (CAD) of the laser desorbed ions was accomplished by using the event sequence shown in Figure 6. Residual ions were removed ("quenched") from the analyzer cell by applying a +15 V potential on one trapping plate and a −15 V potential on the other trapping plate. After the quench pulse, a focused laser pulse desorbed the ions, and a time delay of 1 s was introduced to allow time to pump away desorbed neutrals and thermalize the trapped ions before the CAD pulse. The intact pyridinium cations were translationally excited by irradiation with a 100 μs radio frequency (RF) pulse placed on the excitation plates at the ion's resonance frequency.[50] A collision time of 50 ms was introduced to allow time for collisions with neutral argon molecules at a pressure of 1×10^{-5} Torr (uncorrected ionization gauge pressure). The RF amplitude was varied over a range 1–7 V (peak-to-peak) such that from 0 to ca. 90% CAD occurred.

The standard laser desorption interface supplied by the manufacturer was used. As shown in Figure 7, infrared radiation from a Lumonics TE 860 grating-tuned pulsed CO_2 laser entered the vacuum chamber through a ZnSe window and was focused by a ZnSe lens of 1.25-cm diameter and 5-cm focal length onto a solid probe with a tip modified for laser desorption. The pulsed CO_2 laser produced 1.5 J in a pulse of 1 μs duration at a wavelength of 10.61 microns wavelength and had an unfocused 2 × 3 cm rectangular beam shape. The estimated laser desorption power density was 1×10^8 W/cm^2.

The samples (1–5 mg of the bromide, chloride, perchlorate, or tetrafluoroborate salt) were dissolved in ethanol or methanol (3–5 mL) and deposited on the stainless steel probe tip with a micropipette. The solid probe was inserted into the vacuum chamber, which was then evacuated to a pressure of $1-2 \times 10^{-8}$ Torr before addition of argon. Wide range mass analysis indicated that the samples were of high purity. The intact pyridinium cation was usually the most abundant peak in the positive ion mass spectrum, and the counter anion (either Br^-, Cl^-, ClO_4^-, or BF_4^-) could be detected in the negative ion mass spectrum. No difference in the positive ion mass spectra was observed for any of the counter anions.

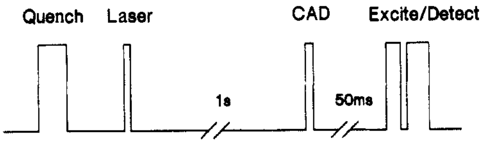


Figure 6. Typical event sequence used for collisionally activated dissociation of laser desorbed ions.

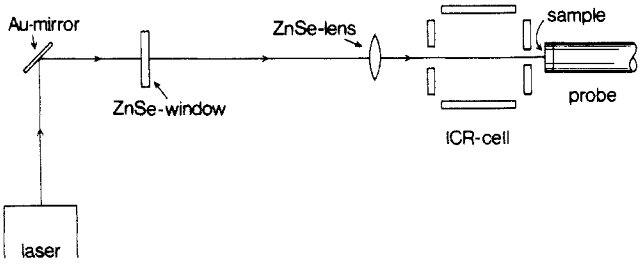


Figure 7. Experimental setup for laser desorption studies.

Calculations of the Heats of Formation. Calculations were performed by the AM1 method[66] with the MOPAC program with complete geometry optimization (Version 3.0)[87] on a MicroVAX II computer. Standard bond lengths and bond angles were taken as the starting points. Planarity of the phenyl and pyridine rings and C_{2v} symmetry of pyridine rings were assumed, but the conformations of CH_2, CH_3, OCH_3, and NO_2, e.g., were optimized.

Preparation of Pyridinium Salts. General Procedure. Method A. To the corresponding alkyl halide (0.01 mol) in dry nitromethane (3 mL) was added the dry pyridine (0.79 g, 0.01 mol). The mixture was stirred under the conditions specified in Table I and then diluted with diethyl ether (30 mL) to give the crude salt, which was recrystallized from the solvent given in Table I. The very hygroscopic pyridinium halides were changed to perchlorates by addition of 70% perchloric acid to an ethanolic solution of the halide. The perchlorates were recrystallized from the solvent given in Table I. **1-(1-Benzotriazolylmethyl)pyridinium Chloride (1r).** Anal. Calcd for $C_{12}H_{11}ClN_4$: C, 58.42; H, 4.49; N, 22.71. Found: C, 58.29; H, 4.44; N, 22.81. **1-(*p*-Chlorobenzyl)pyridinium Chloride (1l).** Anal. Calcd for $C_{12}H_{11}Cl_2N{\cdot}0.5H_2O$: C, 55.86; H, 5.12; N, 5.43. Found: C, 55.83; H, 5.08; N, 5.43.

Method B. To 2,4,6-triphenylpyrylium tetrafluoroborate[41] or perchlorate[42] (1.3 g, 0.005 mol) in dichloromethane (30 mL) was added the corresponding amine (0.005 mol), and the mixture was stirred at 22 °C for 48 h.[88] The 1-substituted-2,4,6-triphenylpyridinium tetrafluoroborates were recrystallized from ethanol. **1-(*p*-(Methylphenyl)ethyl)-2,4,6-triphenylpyridinium tetrafluoroborate**: mp 191–192 °C. Anal. Calcd for $C_{32}H_{28}BF_4N$: C, 74.87; H, 5.50; N, 2.73. Found: C, 74.69; H, 5.58; N, 2.67. **1-(*p*-(Methoxyphenyl)ethyl)-2,4,6-triphenylpyridinium tetrafluoroborate**: mp 127–129 °C. Anal. Calcd for $C_{32}H_{28}BF_4NO$: C, 72.60; H, 5.33; N, 2.65. Found: C, 72.49; H, 5.36; N, 2.67.

The 1-substituted-2,4,6-triphenylpyridinium tetrafluoroborate (**1g**) was heated at reflux in pyridine (10 mL) to give the 1-substituted pyridinium tetrafluoroborate,[43] which was recrystallized from ethanol (mp and yields are given in Table I). **1-(*p*-(Methylphenyl)ethyl)pyridinium Tetrafluoroborate (1l).** Anal. Calcd for $C_{14}H_{16}BF_4N$: C, 58.98; H, 5.66; N, 4.91. Found: C, 58.6; H, 5.48; N, 5.20.

1-(*p*-(Methoxyphenyl)ethyl)pyridinium Tetrafluoroborate (1k). Anal. Calcd for $C_{14}H_{16}BF_4NO$: C, 55.85; H, 5.36; N, 4.65. Found: C, 56.23; H, 5.35; N, 4.50.

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