Dynamics of Proton Transfer from Radical Cations. Addition−Elimination or Direct Proton Transfer?

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Abstract: Kinetic studies including the evaluation of deuterium kinetic isotope effects and Arrhenius activation energies implicate an addition−elimination mechanism for the proton transfer reaction between 9-methylanthracene radical cation and 2,6-lutidine in acetonitrile−Bu_4NPF_6 (0.1 M) and in dichloromethane−Bu_4NPF_6 (0.2 M). Isotopic substitution of D for H at the 10-position results in inverse deuterium kinetic isotope effects (k_H/k_D) equal to 0.83 due to nucleophilic attack on the radical cation by 2,6-lutidine. Primary k_H/k_D of 3.5−5.9 were observed for D_3 substitution in the 9-methyl group. The addition−elimination mechanism involves unimolecular rearrangement of the initially formed adduct to give the product of proton transfer, 9-anthracenylmethyl radical. Oxidation of the latter followed by reaction with 2,6-lutidine affords *N*-(9-anthracenylmethyl)-2,6-lutidinium ion, which was isolated as the perchlorate salt. A comparison of kinetic data from reactions of both 9-methyl and 9,10-dimethylanthracene radical cations with pyridine and 2,6-lutidine results in the conclusion that in the absence of severe steric effects, radical cation−nucleophile combination is kinetically favored over direct proton transfer for these radical cations.

The dynamics of radical cation - nucleophile combination reactions[1−15] as well as radical cation proton transfer reactions[16−31] have been studied intensely for some time. The details of the former have been actively debated yet the mechanism and energetics of these reactions have not been generally agreed upon. On the other hand, the mechanism of the latter is generally accepted to involve a bimolecular reaction between radical cation ($R-H^{•+}$) and base (B) to generate the corresponding neutral radical and the conjugate acid of the base (eq 1). The energetics of reaction 1 are most often highly favorable
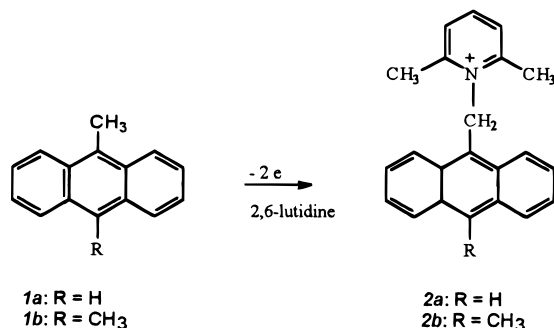
$$R-H^{•+} + B \rightarrow R^{•} + B-H^{+} \tag{1}$$

because of the strongly acidic nature of the radical cations.[25,28,32−37] The experimental evidence upon which this mechanism is based usually consists of the identity of the products of the reaction, the observation of second-order kinetics, and deuterium kinetic isotope effects. However, none of this evidence rules out an alternative mechanism involving reversible covalent adduct formation followed by elimination of BH^+ (eqs 2 and 3). We now report evidence that implicates

$$R-H^{•+} + B \rightleftharpoons (R-H^{•})-B^{+} \tag{2}$$

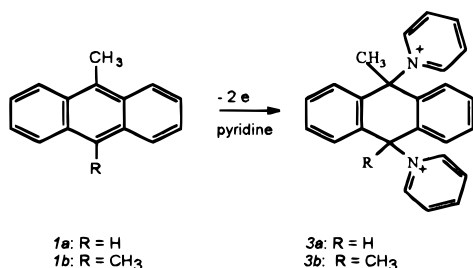$$(R-H^{•})-B^{+} \rightarrow R^{•} + BH^{+} \tag{3}$$
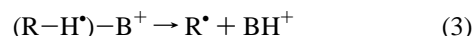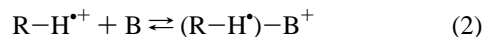
the addition−elimination mechanism for proton transfer during reactions of radical cations derived from 9-methylanthracene (**1a**) and possibly 9,10-dimethylanthracene (**1b**) with 2,6-dimethylpyridine (2,6-lutidine).

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Scheme 1

1a: R = H
1b: R = CH₃

2a: R = H
2b: R = CH₃

Scheme 2

1a: R = H
1b: R = CH₃

3a: R = H
3b: R = CH₃

Scheme 3

3a: R = H
3b: R = CH₃

4b: R = CH₃

4a: R = H

Results

Products of Reactions between Methylanthracene Radical Cations and Pyridines. Exhaustive electrolytic oxidation of both **1a** and **1b** in acetonitrile−Bu₄NPF₆ (0.1 M) in the presence of 2,6-lutidine resulted in the consumption of 2.0 faradays/mol, and the only products (**2a** and **2b**) observed were those derived from proton transfer from the methyl substituents (Scheme 1). The structures (**2a** and **2b**) were assigned from the ¹H NMR spectra (see Experimental Section). Under the same conditions in the presence of pyridine, only products (**3a** and **3b**) derived from attack of the nucleophile at ring positions were observed for either **1a** or **1b** (Scheme 2). The structures of **3a** and **3b** were assigned on the basis of the following evidence:

(i) No oxidation peaks in the potential region expected for substituted anthracenes were observed for the electrolyte solutions after exhaustive oxidation of the substrates which rules out **4a** and **4b** as the products of the electrolysis reactions.

(ii) No ¹H NMR signals were observed in the spectrum of the crude product in the region expected for −CH₂− groups of **4b** ($\delta \approx 6.6-6.8$).

(iii) The products of the electrolysis reactions were not stable in acetonitrile solution and, upon standing, underwent elimination reactions to give **4a** and **4b** (Scheme 3).

(iv) No primary kinetic isotope effects were observed for the reactions of the radical cations derived from **1a** and **1b** with pyridine.

The most characteristic feature of the ¹H NMR spectra of products expected for proton transfer (**2a**, **2b**, and **4b**) is the signal (s, 2H) due to the benzylic protons (δ 6.6−6.8). This signal appears in a spectral region uncomplicated by other signals. This, along with the fact that **2a** could be prepared by an independent method for spectral comparison, facilitated identification of the products which could not be isolated in sufficiently pure form for more detailed analysis.

Voltammetry of Methylanthracenes. In the absence of added bases or nucleophiles nearly reversible cyclic voltammetry (CV) behavior is observed for both **1a** and **1b** in dichloromethane−Bu₄NPF₆ (0.2 M) at voltage sweep rates lower than 1 V/s, indicating that the corresponding radical cations are long-lived under these conditions. In acetonitrile−Bu₄NPF₆ (0.1 M),
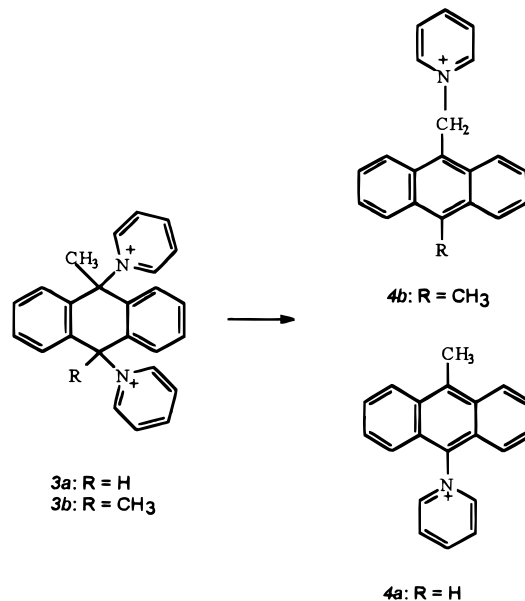
Table 1. Rate Constants for the Reactions of Methylanthracene Radical Cations with Pyridines

radical cation	base	second-order rate Constant (M⁻¹ s⁻¹)[a] in	
		AN-Bu₄NPF₆ (0.1 M)	DCM-Bu₄NPF₆ (0.2 M)
1a•⁺	pyridine	1.5×10^7	1.2×10^7
		(8.0×10^6)	(1.4×10^7)
1a•⁺	2,6-lutidine	4.6×10^6	1.5×10^6
			(1.6×10^6)
1b•⁺	pyridine	3.6×10^6	5.2×10^5
1b•⁺	2,6-lutidine	1.9×10^3	8.7×10^3

[a] At 298 K, values in parentheses obtained by using the prepeak method and all others by DCV.

reversible CV response requires sweep rates of about 10 V/s for the oxidation of **1a** and about 1 V/s for **1b**. The reversible electrode potentials for the oxidation of **1a** and **1b** in acetonitrile−Bu₄NPF₆ (0.1 M), are 1.298 (**1a**) and 1.200 (**1b**) V *vs* the NHE, respectively.

The number of electrons transferred during oxidation of **1a** and **1b** in the presence of both pyridine and 2,6-lutidine was determined from the ratio of the peak height for the oxidation of the substrate (1.0 mM) in the absence and the presence (10− 100 mM) of the heterocyclic compounds. The peak current ratios (R_{pc}), measured at low voltage sweep rates where the reactions are complete during the time of the experiment, were observed to be very close to 2 (1.89−2.12) for the reactions of the radical cations of **1a** and **1b** with both pyridine and 2,6-lutidine.

Kinetics of Reactions between Methylanthracene Radical Cations and Pyridines. The kinetics of the reactions between **1a**•⁺ and **1b**•⁺ with pyridine and 2,6-lutidine were studied with both derivative cyclic voltammetry (DCV)[38] and the prepeak method.[39] The latter method is especially useful since the prepeak is only observed for rapid second-order reactions and the mere observation of the response provides the rate law for the reaction. Kinetic data obtained in both solvent systems are summarized in Table 1. Rate constants shown in parentheses were obtained with the prepeak method while the others were obtained by DCV. Activation parameters and deuterium kinetic isotope data are summarized in Table 2.

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Table 2. Arrhenius Activation Energies and Deuterium Kinetic Isotope Effects for Radical Cation Reactions with Pyridines[a]

reactant pair	E_a/kcal/mol	deuterium labeled substrate	k_H/k_D
1a[•+]/pyridine	2.7 (3.0)	**1a**-*1*	0.84
1a[•+]/2,6-lutidine	−1.3 (−6.0)	**1a**-*1*	0.83 (0.87)
1a[•+]/pyridine	−0.9 (−3.5)	**1a**-2	1.02
1a[•+]/2,6-lutidine	−1.3 (−6.0)	**1a**-2	5.9 (3.5)
1b[•+]/pyridine	−0.9 (−3.5)	**1b**-*1*	1.2 (1.2)
1b[•+]/2,6-lutidine	0.4 (5.9)	**1b**-*1*	17.8 (13.9)

[a] Data obtained in acetonitrile−Bu$_4$NPF$_6$ (0.1 M). Data in parentheses obtained in dichloromethane−Bu$_4$NPF$_6$ (0.2 M).

Discussion

In the past, we have observed that both deuterium kinetic isotope effects and apparent Arrhenius activation energies provide very effective mechanistic criteria for the study of radical ion reactions. Nucleophilic attack on a radical cation at a ring position bearing a hydrogen atom gives rise to a characteristic inverse deuterium kinetic isotope effect. We have consistently found k_H/k_D ranging from 0.7 to 0.9 for radical cation−nucleophile combination reactions.[7] This isotope effect is a consequence of the hybridization change from sp^2 to sp^3 of the carbon atom undergoing nucleophilic attack.[40] Very small or negative Arrhenius activation energies are commonly observed for both radical cation−nucleophile combination[7] and radical cation proton transfer reactions.[22,31] For example, during a study[22] of the aryl proton transfer reaction between 9-phenylanthracene radical cation and 2,6-di-*tert*-butylpyridine an Arrhenius activation energy of −7 kcal/mol was observed for this relatively slow second-order reaction (rate constant of 130 M^{-1} s^{-1}). We have interpreted this result as well as many other comparable results to indicate that the reaction takes place in two steps: reversible formation of a complex (with negative $\Delta H°$) followed by irreversible proton transfer.

Reactions of Methylanthracene Radical Cations with Pyridine. The reactions of both **1a**[•+] and **1b**[•+] with pyridine are radical cation−nucleophile combination reactions. The evidence for this conclusion includes the following:

(i) The products observed for the primary reactions are the addition products, **3a** and **3b**.

(ii) Both reactions follow second-order kinetics.

(iii) An inverse deuterium kinetic isotope effect (0.84) was observed upon substitution of the 10-H of **1a** with D.
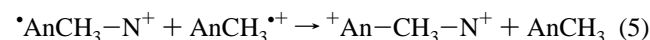
(iv) β-Secondary kinetic isotope effects ($k_H/k_D = 1.2$) were observed for the reactions between **1b**(d_6)[•+] in both acetonitrile and dichloromethane.

Reactions of Methylanthracene Radical Cations with 2,6-Lutidine. We will first look at the reactions of the radical cation giving the most straightforward results (**1b**[•+]) before discussing the more interesting results obtained for **1a**[•+]. The product studies as well as the deuterium kinetic isotope effects for the reactions of **1b**[•+] with 2,6-lutidine appear to support a radical cation proton transfer mechanism. The fact that the reaction is 2 to 3 orders of magnitude slower than the reaction of **1b**[•+] with pyridine could be taken to be a consequence of radical cation−nucleophile combination being intrinsically more rapid than radical cation deprotonation. This ratio for the reactions of 9-phenylanthracene radical cation with the two nucleophiles, reactions which take place by rate determining attack of the

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(42) 9,10-Dihydroanthracene derivatives are known to exist in boat-like conformations (see ref 43 and citations therein).

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nucleophile at the unsubstituted 10-position, is equal to 10^3, *i.e.* in the same range as that for the reactions of **1b**[•+].[7] The apparent Arrhenius activation energy is more positive for the reaction of **1b**[•+] with 2,6-lutidine in dichloromethane than in acetonitrile but perhaps smaller than would be expected for the single step proton transfer reaction (eq 1). On the other hand, large primary deuterium kinetic isotope effects were observed, suggesting quantum mechanical tunneling for the proton transfer reaction.

Substitution of D for H at the 10-position of **1a**[•+] is accompanied by inverse deuterium kinetic isotope effects for the reactions with both pyridine and 2,6-lutidine. This implicates attack by the nucleophile at the 10-position during or prior to the rate determining steps of the reactions. When the nucleophile is pyridine this result is also consistent with the observation of the corresponding adduct as the sole product of the reaction. When 2,6-lutidine is the reactant the product is the side-chain oxidation product, which could arise from either addition−elimination or the direct attack at a side-chain proton. The latter mechanism is inconsistent with the inverse deuterium kinetic isotope effect. The most novel feature of these data is that not only an inverse deuterium kinetic isotope effect is observed upon isotopic substitution of the 10-H but also a primary deuterium kinetic isotope effect is brought about by D$_3$ substitution at the 9-methyl group. The negative apparent Arrhenius activation energies also implicate the addition−elimination reaction for the reaction of **1a**[•+] with 2,6-lutidine.

For both the inverse and the primary deuterium kinetic isotope effects to be observed, it is apparent that both steps giving rise to them must take place before the second electron transfer (which is required for product formation) occurs. The two possibilities for the second electron transfer step involve the oxidation of either the 9-anthracenylmethyl radical (An−CH$_2$[•]) or the adduct radical ([•]AnCH$_2$−N$^+$), where N is 2,6-lutidine, by 9-methylanthracene radical cation, AnCH$_3$[•+] (eqs 4 and 5).

$$AnCH_2^{\bullet} + AnCH_3^{\bullet+} \rightarrow AnCH_2^+ + AnCH_3 \quad (4)$$

$$^{\bullet}AnCH_3-N^+ + AnCH_3^{\bullet+} \rightarrow {}^+An-CH_3-N^+ + AnCH_3 \quad (5)$$

Both of these reactions are expected to be highly exergonic and can be considered to be essentially irreversible.[41] If either of these reactions were rate determining, kinetics second-order in radical cation would be observed. Since the reaction between AnCH$_3$[•+] and 2,6-lutidine follows rate law (6), neither of these

$$d[AnCH_3^{\bullet+}]/dt = -k_{obs}[AnCH_3^{\bullet+}][2,6\text{-lutidine}] \quad (6)$$

reactions can take place before the rate determining step. Therefore, the mechanism has to account for both the inverse and the primary kinetic isotope effects either before or during a step preceeding electron transfer. Since this is the evidence that unequivocally rules out the simple bimolecular proton transfer mechanism (eq 1), we reemphasize this point, both kinetic isotope effects are brought about by a reaction step, or reaction steps, at the one-electron oxidation state of 9-methylanthracene.

The only mechanism apparent to us that takes into account not only the observation of an inverse deuterium kinetic isotope effect upon isotopic substitution of the 10-H but also a primary deuterium kinetic isotope effect brought about by D$_3$ substitution at the 9-methyl group is shown in Scheme 4. The first step in this mechanism is nucleophilic attack by 2,6-lutidine at the 10-position of **1a**. This step is responsible for the inverse deuterium kinetic isotope effect. This is then followed by a unimolecular elimination of 2,6-lutidinium ion from the adduct to generate

Scheme 4
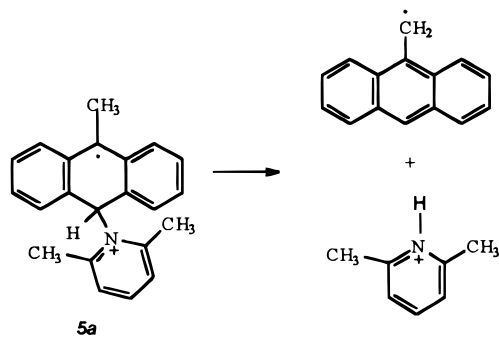
the 9-anthracenylmethyl radical. The latter can then participate in reaction 4 to give the observed product of the reaction, *N*-(9-anthracenylmethyl)-2,6-lutidinium ion.

The transition state for the elimination reaction most likely involves a boat-like conformation of the central ring of **5a**.[42] A conformer with both the 9-methyl group and the 10-lutidinium moiety situated in axial positions (structure **6** in which only the central anthracene ring is shown) appears to have the most
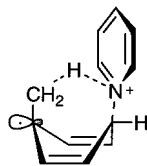
favorable geometry for the unimolecular rearrangement. The hybridization of the 2,6-lutidinium ion nitrogen most likely remains sp^2 in the transition state. Rehybridization of the nitrogen to sp^3 would appear to be more favorable geometrically but less favorable energetically. The fact that an inverse kinetic isotope effect is observed upon deuterium substitution of the 10-H implicates concerted bond breaking and formation with an early transition state for the elimination reaction (Scheme 4). An early transition state is also supported by the observation of relatively large primary deuterium kinetic isotope effects for D$_3$ substitution at the 9-methyl group.[44]

Although experimental data are not available for evaluation of the rate constant for the elimination of 2,6-lutinium ion from **5a** (reaction 8) or for the evaluation of the rate and equilibrium constants for reaction 7, we can estimate an approximate lower limit value ($\approx k_{obs}$[2,6-lutidine]$_o$) by assuming that reaction 7 does not reach equilibrium and that the initial rates of formation of 7 and reaction 8 of **5a** are approximately equal. An initial

$$\mathbf{1a}^{\bullet+} + \text{2,6-lutidine} \rightleftarrows \mathbf{5a} \qquad (7)$$

$$\mathbf{5a} \rightarrow \mathbf{7} \qquad (8)$$
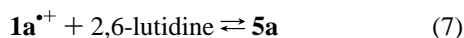
concentration of 2,6-lutidine of 0.5 mM and $k_{obs} = 1.5 \times 10^6$ M^{-1} s^{-1} leads to $(k_8)_{min} \approx 750$ s^{-1}. We have been unable to find reports in the literature of rapid rearrangements similar to reaction 8.

Conclusions

Both $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$ undergo radical cation−nucleophile combination reactions with pyridine. The reaction between $\mathbf{1a}^{\bullet+}$ and 2,6-lutidine takes place by an addition−elimination mechanism rather than by simple proton transfer. We conclude that the data do not differentiate between the direct proton transfer and the addition−elimination mechanisms for reaction of $\mathbf{1b}^{\bullet+}$ with 2,6-lutidine.

Two fundamental conclusions can be drawn from the work presented here. The first is that for the systems studied, in the absence of severe steric effects, radical cation−nucleophile combination appears to be kinetically more favorable than direct proton transfer even though the latter is highly exergonic.[45] The second is that, because of the relative ease of the two primary reactions, *i.e.,* nucleophilic attack and direct proton transfer, the addition-elimination mechanism for radical cation proton transfer reactions can dominate over the single step proton transfer reaction. Since the addition step cannot readily be detected in most cases, experimental evidence most often does not differentiate between the two mechanisms.

Experimental Section

Materials. Reagent grade acetonitrile was distilled from P$_2$O$_5$ before being passed through a column of active neutral alumina to remove water and protic impurities. Dichloromethane, after passing through active neutral alumina, was used without further purification. Tetrabutylammonium hexafluorophosphate (Aldrich) was recyrstallized from dichloromethane−ether before use. 9-Methylanthracene and 9,10-dimethylanthracene (Aldrich) were recrystallized from 2-propanol before use. Pyridine and 2,6-lutidine (Aldrich) were distilled under reduced pressure. 9-Chloromethylanthracene was used as received from Aldrich.

9-Methylanthracene-*10-d* was prepared from the reaction of 9-methyl-10-bromoanthracene by halogen−lithium exchange with *tert*-butyllithium under a nitrogen atmosphere followed by quenching with deuterium oxide in THF at −78 °C. 9-Methyl-10-bromoanthracene was obtained by bromination of 9-methylanthracene in CCl$_4$.

9-Methyl-*d$_3$*-anthracene was prepared according to a literature procedure[48] with methyl-*d$_3$*-magnesium iodide as the Grignard reagent.

9,10-Dimethyl-*d$_6$*-anthracene was prepared according to the method of Fieser[49] with methyl-*d$_3$*-magnesium iodide as the Grignard reagent.

Instrumentation and Data Handling Procedures. Cyclic and linear sweep voltammetry were performed with a Princeton Applied Research (Princeton, NJ) Model 173 potentiostat/galvanostat driven by a Hewlett Packard 3314A function generator. After passing through a Stanford Research Systems, Inc. Model SR640 dual channel low pass filter the data were recorded on a Nicolet Model 310 digital oscilloscope with 12-bit resolution. The oscilloscope and function generator were controlled by an IBM AT compatible personal computer *via* an IEEE interface. The current−potential curves were collected at selected trigger intervals to reduce periodic noise,[50] and 20 curves were averaged before being treated with a frequency domain low pass digital filter and numerical differentiation.

Cyclic Voltammetry Measurements. A standard three-electrode one compartment cell was used for all kinetic measurements. Positive feedback IR compensation was used to minimize the effects of uncompensated solution resistance. Reference electrodes were Ag/AgNO$_3$ (0.01 M) in acetonitrile constructed in the manner described by Moe.[51] The working electrodes, 0.2−0.8 mm Pt, were prepared by sealing wire in glass and polishing to a planar surface as described previously.[52] The working electrodes were cleaned before each series of measurements with a fine polishing powder (Struers, OP-Alumina Suspension) and wiped with a soft cloth. The cell was immersed in a water bath controlled to 25 ± 0.2 °C.

Kinetic Measurements. Rate constants were obtained by comparing derivative cyclic voltammetry[38] or prepeak data[39] to theoretical data

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(45) The pK_a values of $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$ in DMSO have been estimated to be equal to −6.5 and −5.0, respectively.[37] Addition of 9 pK_a units for the change to acetonitrile as solvent[46] and taking into account the known pK_a of the pyridines[47] results in the conclusion that both reactions are highly exergonic ($\Delta G°$ equal to −9.8 and −8.3 kcal/mol, respectively).

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obtained by digital simulation.[53] The reactions were studied under second-order conditions by using solutions containing substrate (1.0 mM)/nucleophile (2.0 mM) for DCV measurements and substrate (1.0 mM)/nucleophile (0.5 mM) for prepeak measurements.

Product Studies. The electrolyses were carried out in acetonitrile containing LiClO$_4$ (0.1 M) as the supporting electrolyte. The use of the inorganic salt rather than the usual tetraalkylammonium salts was necessary to avoid difficulties with separating the ionic products from the electrolyte. The reactions were carried out in H cells containing about 20 mL in each compartment of solutions of 0.5 mmol of substrate and 1.5 mmol of the appropriate nucleophile. A constant current was passed for a time sufficient for 2 faradays/mol of substrate before the electrolysis was discontinued.

Conditions were not found where crystalline products could be obtained. Solid residues were obtained after evaporation of solvent, and separation from the electrolyte was achieved by partitioning between aqueous and organic phases followed by removal of the organic solvent. The residue was then taken up in anhydrous acetonitrile or acetonitrile/dichloromethane and the pyridinium salts were precipitated slowly by the dropwise addition of diethyl ether. This procedure, which served to remove unreacted starting materials, was repeated two or more times.

The ^{1}H NMR spectra of the residues obtained from the reactions of both **1a** and **1b** with pyridine, measured immediately after dissolving in CD$_3$CN, were observed to be consistent with those of structures **3a** and **3b**. However, upon standing in CD$_3$CN at ambient temperature, changes in the spectra were observed over a period of about 24 h, indicating that the initial products were converted to **4a** and **4b**. The structures of **4a** and **4b** were assigned from the ^{1}H NMR spectra of the solutions after standing for about 2 days. The interpretation of ^{1}H NMR

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spectra of the pyridinium salts obtained by electrolysis was greatly simplified by the comparison of those prepared from pyridine with those from pyridine-d$_5$.

The ^{1}H NMR spectra of the products of electrolytic oxidation of **1a** and **1b** in acetonitrile−LiClO$_4$ (0.1 M) containing 2,6-lutidine were observed to be consistent with structures **2a** and **2b**. The assignment of structure **2a** for the reaction product of **1a** was verified by comparison of the ^{1}H NMR spectrum with that obtained by treating 9-chloromethylanthracene with stoichiometric quantities of 2,6-lutidine and AgClO$_4$ in CD$_3$CN.

^{1}H NMR (CD$_3$CN, 300 MHz) Data for Electrolysis Products. (a) *N*-(10-Methylanthracenyl)pyridinium (4a) perchlorate salt: δ 3.26 (s, 3H), 7.22 (d, 2H), 7.66−7.78 (m, 4H), 8.56 (t, 2H), 8.63 (d, 2H), 9.28 (t, 1H), 9.54 (d, 2H).

(b) *N*-(9-Anthracenylmethyl)-2,6-lutidinium (2a) perchlorate salt: δ 2.58 (s, 6H), 6.78 (s, 2H), 7.52−7.58 (m, 4H), 7.68−7.74 (m, 4H), 8.12−8.18 (m, 2H), 8.21−8.27 (t, 1H), 8.72 (s, 1H).

(c) *N*-(10-Methyl-9-anthracenylmethyl)pyridinium (4b) perchlorate salt: δ 3.20 (s, 3H), 6.73 (s, 2H), 7.62−7.68 (m, 4H), 7.85−7.91 (t, 2H), 8.16−8.22 (m, 2H), 8.38−8.44 (t, 1H), 8.44−8.50 (m, 2H), 8.54−8.57 (d, 2H).

(d) *N*-(10-Methyl-9-anthracenylmethyl)-2,6-lutidinium (2b) perchlorate salt: δ 2.52 (s, 6H), 3.18 (s, 3H), 6.78 (s, 2H), 7.54−7.69 (m, 4H), 7.66−7.71 (d, 2H), 7.75−7.80 (d, 2H), 8.18−8.25 (t, 1H), 8.45−8.50 (d, 2H).