Products of the Reactions between Substituted Anthracene Radical Cations and Nitrogen-Centered Nucleophiles

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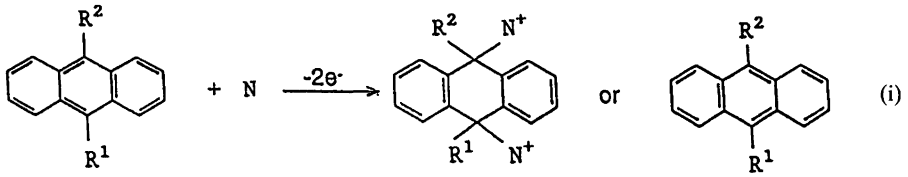
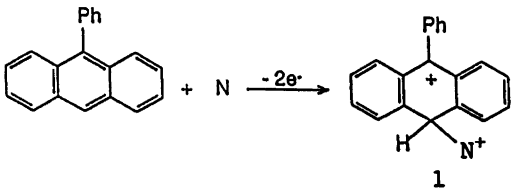
Radical cations derived from anthracene and 9-substituted or 9,10-disubstituted anthracenes react with pyridine and substituted pyridines in aprotic solvents to give either mono- or bis-pyridinium salts. Bis-pyridinium salts were observed when R^1 = R^2 = H. 9-Substituted anthracene radical cations (R^1 = Ph, NO_2, or CN and R^2 = H) react to give mono-pyridinium salts, eqn. (i). The most important factors influencing



(i)

the product distribution are the steric environment at the 9-position after the initial attack by the nucleophile at the 10-position and the electronic effect of substituents at the latter position of the anthracene nucleus. In the case of the parent anthracene radical cation, attack at the 10-position leaves an unsubstituted 9-position for further attack resulting in the eventual formation of the bis-pyridinium salt. On the other hand, radical cations derived from 9-substituted anthracenes lead to intermediates in which the 9-position is hindered toward nucleophilic attack and an acid–base reaction leading to mono-pyridinium salt prevails.

Although a large number of papers have dealt with the mechanism of the reactions of anthracene radical cations with nucleophiles,[1–16] little attention has been paid to the products of the reactions.[17,18] Products have been characterized from the reactions of anthracene[17] and 9,10-diphenylanthracene[18] with pyridine. In both of these cases the products observed corresponded to the oxidative addition of pyridine to the 9,10-positions to give the bis-pyridinium salts [(eqn. 1)]. That this is not the only reaction pathway available when one of the reactive 9- or 10-positions is unsubstituted has been shown by a cyclic voltammetry study of the oxidation of 9-phenylanthracene in acetonitrile



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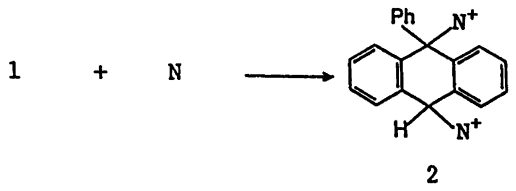

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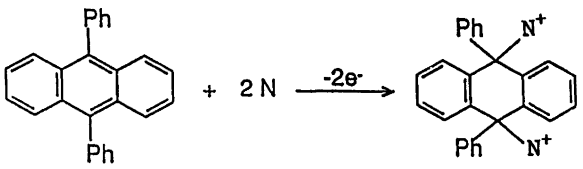

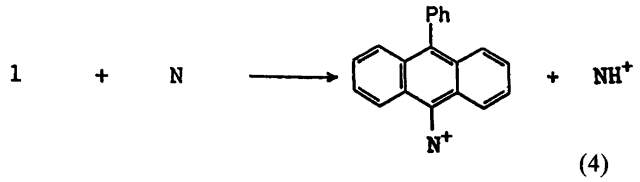

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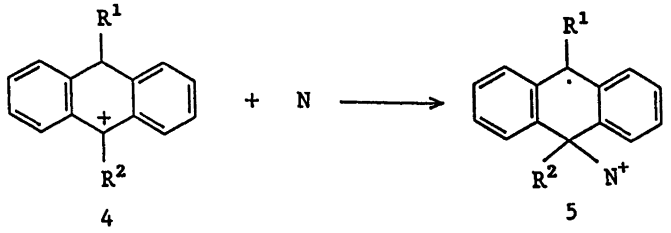
in the presence of dimethylpyridines.[2] The initial steps (2) in the reaction were invariably observed to produce the carbocation **1**. The manner in which **1** partitions between the two product-forming channels to give **2** or **3** was observed to depend strongly upon the substitution pattern of the dimethylpyridines. When the nucleophile was 3,5-dimethylpyridine nuclophilic attack on carbocation **1** predominated to give the adduct **2**. Highly hindered 2,6-dimethylpyridine was observed to act exclusively as a base toward **1** to give **3**. The less hindered 2,5-dimethylpyridine was observed to act both as a nucleophile and as a base to give a mixture of **2** and **3**.

Product purification proved to be a major problem. Conditions were not found where crystalline products could be obtained. A solid residue was obtained after evaporation of acetonitrile and separation from the electrolyte 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 was repeated two or more times. In some cases chromatographic separations on silica gel, developing with acetone/acetonitrile was necessary to afford products sufficiently



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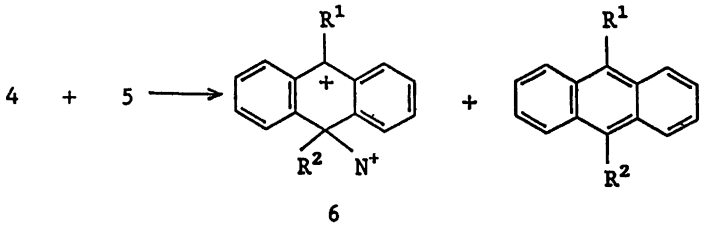

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Results and discussion

The initial step in the radical cation – nucleophile combination reaction is not the most decisive in determining the nature of the products. Since this step generates an unstable free radical (**5**), illustrated below for the reaction of a substituted anthracene radical cation with a nucleophile, eqn. (5), a second electron transfer eqn. (6), is necessary to form the cationic intermediate (**6**) which takes part in the product-forming reactions.

Substrates used in this study include anthracene, 9-cyanoanthracene, 9-nitroanthracene and 9-phenylanthracene. Pyridinium salts were isolated using pyridine, 2-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine and 4-cyanopyridine as the nucleophiles (Table 1).

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 time sufficient for 2 F mol^{-1} of substrate before discontinuing the electrolysis.

Table 1. Products obtained from radical cation – nucleophile combination reaction in acetonitrile.

Substrate	Nucleophile	Isolated yields (%)[a]	
		Addition	Elimination
Anthracene	Pyridine	64	
	2-Methylpyridine	42	
	4-Methylpyridine	34	
	4-Cyanopyridine	53	
9-Cyanoanthracene	Pyridine		73
	2-Methylpyridine		70
	4-Methylpyridine		57
	4-Cyanopyridine		70
9-Nitroanthracene	Pyridine		68
9-Phenylanthracene	Pyridine		35
	2-Methylpyridine		70
	4-Methylpyridine		54
	4-Cyanopyridine		76
	2,6-Dimethylpyridine		64

[a]Addition refers to the formation of the 9,10-bis-pyridium salt and elimination to the formation of the 10-substituted monopyridinium salt.

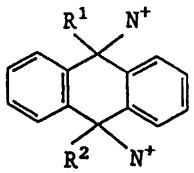
pure for ^{1}H NMR analysis. The products appeared pure by ^{1}H NMR but sufficiently high purity for satisfactory elemental analysis was not achieved for any of the salts.

The interpretation of ^{1}H NMR spectra of the pyridinium salts was greatly simplified by the comparison of salts prepared using pyridine with those from pyridine-d_5. Comparison of the spectra allowed unequivocal assignments of the protons on the pyridine ring.

The bis-pyridinium salts derived from anthracene exist as mixtures of isomers. The two pyridine moieties can exist as axial/axial, equatorial/equatorial or axial/equatorial. The ^{1}H NMR spectra are indicative of more than one isomer in all cases but we were unable to determine the proportions of isomers present.

Constant-current coulometry using linear-sweep voltammetry detection of the disappearance of substrate[19] indicated that under these conditions, i.e. concentrations of 1.0 mM (substrate) and 3.0 mM (nucleophile) using low current densities, the reactions are highly efficient (2.0 F mol^{-1}). However, on a preparative scale, where concentrations were increased by greater than an order of magnitude, the yields of isolated products were typically about 70% based on charge consumed. Unchanged starting material was invariably present in the cell after the theoretical amount of charge for a 2 e$^-$ process had been consumed. The lower efficiency on the larger scale was a consequence of the scale-up and no attempts were made to optimize the reaction conditions.

In all cases a single product was identified by ^{1}H NMR analysis. The structures of the products were either the bis-pyridinium salts (**7**) resulting from nucleophilic attack on the cation **6** or the mono-pyridinium salt **8** formed by the proton transfer from **6** to the nucleophilic base. Bis-pyridinium salts (**7**) were observed only with anthracene as the substrate. Anthracene was converted into **7**, independent of the identity of the pyridine nucleophile. Radical cations generated from the remaining substrate, 9-cyanoanthracene, 9-nitroanthracene and 9-phenylanthracene, were transformed into the mono-pyridinium salts **8** upon 2 e$^-$ oxidation in the presence of the pyridine nucleophiles.



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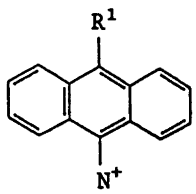

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Of the substrates studied only unsubstituted anthracene resulted in the formation of **7**. On this basis we conclude that both steric and electronic effects of the 9-substituents can favor the proton transfer reactions and result in **8**. When the substituent is phenyl the predominant effect is likely to be steric, hindering attack at the 9-position. When the substituent is the linear CN the steric effect is not expected to be important, yet proton transfer appears to be the exclusive pathway. This is readily explained by the effect on the acidity of the proton being transferred of the strongly electron-withdrawing substituent. Both the steric and the electronic effect of the NO_2 substituent favor proton transfer resulting in **8**.

Experimental

General. All ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts are reported relative to the solvent, CD_3CN (1.93 ppm). The protons of the pyridinium salts fall into three groups, those attached to the anthracene nucleus designated as Anth (anthryl), those of the phenyl ring when PAH is the substrate designated as Ph (phenyl) and those attached to pyridine nucleus, Pyr (pyridyl). Melting points were measured in capillary tubes with a Thomas capillary melting point apparatus and are uncorrected. Melting points are only reported in cases were a sharp melting point was found. Reagent-grade acetonitrile was distilled from P_2O_5 before it was passed through a column of active neutral alumina to remove water and protic impurities. Dichloromethane was distilled from calcium chloride, and treated the same way after the electrolyte had been added. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane–ether before use. Lithium perchlorate (Aldrich) was used as received. 9-Phenylanthracene (Aldrich) and 9-anthracenecarbonitrile (Aldrich) were used without further purification, anthracene (Merck) was recrystallized from isopropyl alcohol and 9-nitroanthracene was prepared according to a published procedure.[20] 10-Phenylanthracene-9-*d* was prepared by $LiAlD_4$ reduction of 9-bromo-10-phenylanthracene, obtained by bromination of 9-phenylanthracene. Anthracene-9,10-d_2 was prepared from 9,10-dibromoanthracene by a halogen–lithium exchange at −78 °C using butyllithium under an atmosphere of nitrogen followed by quenching with D_2O. All pyridines were puri-

Table 2. Fast-atom bombardment mass spectral data of selected pyridinium salts.[a]

Structure	*M* Found (theory)	*M*+1 Found (theory)
9-d_5	306.13 (306.13)	307.13 (307.13)
10	308.87 (309.4)	
11	306.10 (306.10)	307.10 (307.10)
12	435.11 (435.11)	436.11 (436.11)
13	485.10 (485.10)	486.10 (486.10)
14	332.16 (332.43)	
15	357.14 (357.14)	358.14 (358.14)
16	360.23 (360.50)	

[a]Spectra were obtained only on salts judged to be of high purity.

fied the same day prior to use using standard techniques. FAB mass spectral data was provided by Dr. Donald Bethell, University of Liverpool and are summarized in Table 2.

9-Nitro-10-pyridinioanthracene perchlorate (**9**). Isolated yield: 135 mg, 68%; m.p. 214–216°C; ^{1}H NMR: δ 9.04–8.94 (m, 3 H, Pyr), 8.49–8.44 (m, 2 H, Pyr), 8.09 (d, 2 H, J = 8.9 Hz, Anth), 7.89 (t, 2 H, J = 8.9 Hz, Anth), 7.77 (t, 2 H, J = 8.9 Hz, Anth), 7.31 (d, 2 H, J = 8.9 Hz, Anth). The signals in the spectrum were assigned by comparison with that of 9-nitro-10-pyridinio-d_5-anthracene perchlorate.

9-Cyano-10-(4-methylpyridinio)anthracene perchlorate (**10**). Isolated yield: 113 mg, 57%; ^{1}H NMR: δ 8.74 (d, 2 H, J = 6.8 Hz, H-2, H-6, Pyr), 8.59 (d, 2 H, J = 8.7 Hz, H-4, H-5, An), 8.24 (d, 2 H, J = 6.8 Hz, H-3, H-5, Pyr), 7.97–7.92 (m, 2 H, Anth), 7.81–7.76 (m, 2 H, Anth), 7.36 (d, 2 H, J = 8.8 Hz, H-1, H-8, Anth), 2.90 (s, 3 H, CH_3-Pyr).

9-Cyano-10-pyridinioanthracene perchlorate. Isolated yield: 112 mg, 73%; ^{1}H NMR: δ 9.06–8.97 (m, 3 H, H-2, H-6, H-4, Pyr), 8.61 (d, 2 H, J = 8.8 Hz, An), 8.52–8.47 (m, 2 H, H-3, H-5, Pyr), 8.01–7.95 (m, 2 H, Anth), 7.83–7.78 (m, 2 H, Anth), 7.35 (d, 2 H, J = 8.8 Hz, H-1, H-8, Anth). The signals in the spectrum were assigned by comparison with that of 9-cyano-10-pyridinio-d_5-anthracene perchlorate.

9-Cyano-10-(2-methylpyridinio)anthracene perchlorate. Isolated yield: 138 mg, 70%; ^{1}H NMR: δ 8.89–8.84 (m, 1 H, Pyr), 8.71 (d, 1 H, J = 5.7 Hz, Pyr), 8.61 (d, 2 H, J = 9.0 Hz, H-4, H-5, Anth), 8.36 (d, 1 H, J = 8.2 Hz, Pyr), 8.26–8.22 (m, 1 H, Pyr), 7.99–7.93 (m, 2 H, Anth), 7.82–7.76 (m, 2 H, Anth), 7.25 (d, 2 H, J 8.8 Hz, H-1, H-8, Anth), 2.29 (s, 3 H, CH_3-Pyr).

9-Cyano-10-(4-cyanopyridinio)anthracene perchlorate (**11**). Isolated yield: 143 mg, 70%; ^{1}H NMR: δ 9.17 (d, 2 H, J = 7.0 Hz, Pyr), 8.80 (d, 2 H, J = 7.0 Hz, Pyr), 8.60 (d, 2 H, 8.74 Hz, H-4, H-5, Anth), 7.98–7.94 (m, 2 H, Anth) 7.84–7.78 (m, 2 H Anth), 7.39 (d, 2 H, J = 8.8 Hz, H-1, H-8, Anth).

9-Cyano-10-(2,6-dimethylpyridinio)anthracene perchlorate. Isolated yield: 90 mg, 44%; ^{1}H NMR: δ 8.70 (t, 1 H, J = 8.0 Hz, H-4, Pyr), 8.63 (d, 2 H, J = 8.0 Hz, H-3, H-5, Pyr), 8.15 (m, 2 H, J = 8.1 Hz, H-4, H-5, Anth), 7.98 (m, 2 H, Anth), 7.82 (m, 2 H, Anth), 7.23 (m, 2 H, H-1, H-8, Anth), 2.12 (s, 6 H, 2 × CH_3-Pyr).

9,10-Dihydro-9,10-di(4-methylpyridinio)anthracene diperchlorate. Isolated yield: 95 mg, 34%; m.p. 142–144°C; ^{1}H NMR: δ 8.71 (d, 2 H, J = 5.4 Hz, H-2, H-6, Pyr), 8.65 (d, 2 H, H-2, H-6, J = 5.7 Hz, Pyr), 7.95 (d, 2 H, H-3, H-5, J = 5.4 Hz, H-3, H-5, Pyr), 7.85 (d, 2 H, J = 5.7 Hz, H-3, H-5, Pyr), 7.61–7.48 (m, 4 H, Anth), 7.39–7.26 (m, 2 H, Anth), 7.10–7.06 (m, 2 H, Anth), 6.52 (br s, 2 H, H-9, H-10) 2.72, 2.70, 2.62, 2.59 (4 × CH_3-Pyr, *ax/ax, eq/eq* and *ax/eq*).

9,10-Dihydro-9,10-dipyridinioanthracene diperchlorate (**12**). Isolated yield: 170 mg, 64%; m.p. found 152–154°C, lit.[11] 169–171°C. ^{1}H NMR: δ 8.92 (d, 2 H, J = 6.64 Hz, H-2, H-6, Pyr), 8.83 (d, 2 H, J = 6.64 Hz, H-2, H-6, Pyr), 8.69 (t, 1 H, J = 6.64 Hz, H-4, Pyr), 8.60 (t, 1 H, J = 6.64 Hz, H-4, Anth), 8.17 (t, 2 H, J = 6.64 Hz, H-3, H-5, Pyr), 8.10 (t, 2 H, J = 6.64 Hz, H-3, H-5, Pyr), 7.57–7.50 (m, 6 H, Anth), 7.42–7.39 (m, 2 H, Anth), 7.19 (s, 1 H, H-9, *ax/eq*), 7.18–7.13 (m, 1 H, H-10, *ax/eq*).

9,10-Dihydro-9,10-di(2-methylpyridinio)anthracene diperchlorate. Isolated yield: 119 mg, 42%; m.p. 178–179°C; ^{1}H NMR: δ 8.47–8.39 (m, 4 H, Pyr), 8.10 (d, 2 H, J = 7.7 Hz, Pyr), 7.84–7.79 (m, 4 H, H-9 and H-10, + 2 H Pyr), 7.53–7.45 (m, 4 H, Anth), 7.37–7.25 (m, 4 H, Anth), 3.19 and 3.11 (s, 6 H, 2 × CH_3-Pyr, *ax/eq*). H-9 and H-10 were found by comparing the spectrum with that of the identical compound made from anthracene-9,10-d_2.

9,10-Di(4-cyanopyridinio)-9,10-dihydroanthracene diperchlorate (**13**). Isolated yield: 155 mg, 53%; m.p. 157–159°C; ^{1}H NMR: δ 9.00 (d, 4 H, J = 6.2 Hz, H-2, H-6, Pyr), 8.41 (d, 4 H, J = 6.2 Hz, H-3, H-5, Pyr), 7.59–7.55 (m, 6 H, H-9, H-10 + 4 H Anth), 7.49–7.43 (m, 4 H, Anth). H-9 and H-10 were found by comparing the spectra with that of the identical salt prepared from anthracene-9,10-d_2.

10-(4-Methylpyridinio)-9-phenylanthracene perchlorate. Isolated yield: 120 mg, 54%; ^{1}H NMR: δ 8.79 (d, 2 H, J = 6.5 Hz, Pyr), 8.23 (d, 2 H, J = 6.5 Hz, Pyr), 7.78 (d, 2 H, J = 8.6 Hz, An), 7.73–7.46 (m, 9 H, Anth), 7.25 (d, 2 H, J = 8.8 Hz, Anth), 2.90 (s, 3 H, CH_3-Pyr).

9-Phenyl-10-pyridinioanthracene perchlorate (**14**). Isolated yield: 75 mg, 35%; ^{1}H NMR: δ 9.00 (m, 3 H, Pyr), 8.45 (m, 2 H, Pyr), 7.80 (d, 2 H, J = 9.1 Hz, Anth), 7.70–7.47 (m, 9 H, Anth + Ph), 7.23 (d, 2 H, J = 9.1 Hz, Anth). The signals in the spectrum were assigned by comparison with that of 9-phenyl-10-pyridinio-d_5-anthracene perchlorate.

10-(2-Methylpyridinio)-9-phenylanthracene perchlorate (**15**). Isolated yield: 155 mg, 70%; ^{1}H NMR: δ 8.84 (m, 1 H, Pyr), 8.77 (d, 1 H, J = 6.54 Hz, Pyr), 8.36 (d, 1 H, J = 8.1 Hz, Pyr), 8.25 (t, 1 H, J = 6.54 Hz, Pyr), 7.81 (d, 2 H, J = 8.74 Hz, H-4, H-5, Anth), 7.78–7.47 (m, 9 H, Anth + Ph), 7.14 (d, 2 H, J = 8.74 Hz, H-1, H-8, Anth), 2.35 (s, 3 H, CH_3-Pyr).

10-(4-Cyanopyridinio)-9-phenylanthracene perchlorate. Isolated yield: 174 mg, 76%; ^{1}H NMR: δ 9.22 (d, 2 H, J = 7.0 Hz, Pyr), 8.79 (d, 2 H, J = 7.0 Hz, Pyr), 7.73–7.47 (m, 9 H, Anth + Ph), 7.29 (d, 2 H, J = 8.8 Hz, Anth).

10-(2,6-Dimethylpyridinio)-9-phenylanthracene perchlorate (**16**). Isolated yield: 147 mg, 64 %; ^{1}H NMR: δ 8.69 (t, 1 H, J = 8.0 Hz, H-4, Pyr), 8.16 (d, 2 H, J = 8.0 Hz, H-3, H-5, Pyr), 7.82 (d, 2 H, J = 8.8 Hz), 7.73–7.50 (m, 9 H, Anth + Ph), 7.13 (d, 2 H, J = 8.8 Hz, Anth), 2.21 (s, 6 H, 2 × CH_3-Pyr).

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