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Photoinduced Electron Transfer Chemistry of 9-Methylanthracene. Substrate as Both Electron Donor and Acceptor in the Presence of the 1-Ethyl-3-methylimidazolium Ion

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Abstract: Photolysis of 9-methylanthracene (**2a**; 9-CH_3An) in a deoxygenated molten salt consisting of 1-ethyl-3-methylimidazolium chloride (**1**; EMIC) (55 mol %) and $AlCl_3$ at room temperature yielded, in addition to the anti 4 + 4 dimer (**3**), six products, four of which are dimeric (two oxidized [**8** and **9**]; two neutral [**4** and **5**]) and two of which are monomeric (one reduced [**7**]; one neutral [**6**]). The same products were produced in CH_3CN containing **1**. These six products arose by initial electron transfer from 9-MeAn^{*1} to EMI$^+$ to form the radical cation of 9-MeAn and EMI$^\bullet$. The reduced product **7** arose by electron transfer from EMI$^\bullet$ to 9-MeAn. This system thus contained both the radical cation and radical anion of 9-MeAn at different stages of the reaction. Experiments using 9-CD_3An, 2-deuterioEMIC, and 2,4,5-trideuterioEMIC in the molten salt and 9-CH_3An in the presence of *N*-1-butylpyridinium chloride (BPC) (BPC/CH_3CN) and the molten salt BPC [55 mol %]/$AlCl_3$ clarified mechanistic details.

Introduction

Salts have played a prominent role in mechanistic and synthetic organic chemistry.[1] Normal and special salt effects have proven invaluable in elucidating the mechanisms of solvolysis reactions,[2] for example, and $LiClO_4$/ether has found wide use in synthesis in recent years.[3] Because a saturated solution of $LiClO_4$ in ether contains about the same amount of the two components,[4] what constitutes the solute and solvent in $LiClO_4$/ether is unclear. In any event, the saturated solution is approaching the regime of a molten salt.

In spite of the fact that many ionic compounds are liquids only well-above ambient temperature, many organic reactions in molten salts are known.[5] Furthermore, as there are now available several molten salts which are liquids at or below room temperature, e.g., ethylammonium nitrate[6] and admixtures of 1-ethyl-3-methyl-1*H*-imidazolium chloride (**1**; EMIC) and $AlCl_3$,[7] the field of organic reactions in molten salts should blossom in the future.

Only two examples of photochemical reactions in molten salts have been reported in the literature: iron(II) imine complexes in ethylpyridinium bromide/$AlCl_3$ (1:2 mole ratio)[8] and an-

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[†] Deceased March 12, 1995.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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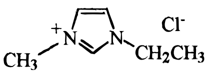
thracene in the Lewis acidic (and basic) EMIC (45 mol %)/$AlCl_3$,[9] both of whose photochemistry are initiated by electron transfer from the excited state of the substrate to an electron deficient component in the solution. This sparseness is unfortunate because molten salts will provide unusual environments for photochemistry, and many of them possess electron deficient components capable of functioning as electron acceptors in photoinduced electron transfer (PET) reactions.[10]

We wish to report at this time on the rich photochemistry of 9-methylanthracene (**2a**; 9-CH_3An) in the Lewis basic room temperature molten salt EMIC (55 mol %)/$AlCl_3$, which yields both the radical cation and radical anion of the substrate at different stages of the reaction, a result not previously seen for a photochemical reaction in fluid solution.



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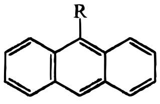

2a R = CH_3
2b R = CD_3

Results and Discussion

Photolysis of anthracene (An) in basic EMIC/$AlCl_3$ afforded the 4 + 4 dimer exclusively;[9] if $An^{+\bullet}$ were formed by electron transfer from An to EMI^+, no net chemistry resulted. On the other hand, 9-$CH_3An^{+\bullet}$, a very strong acid,[11] has a chemical outlet unavailable to $An^{+\bullet}$, i.e., abstraction of a methyl proton by Cl^-, present in large concentration in the basic molten salt, to form HCl and the 9-anthrylmethyl radical (9-$AnCH_2^\bullet$) (eq 1). Thus, the formation of products containing the 9-anthrylmethyl moiety from the photoreaction of **2a** in the molten salt will constitute evidence for the PET reaction.

$$9\text{-}CH_3An^{+\bullet} + Cl^- \rightarrow HCl + 9\text{-}AnCH_2^\bullet \qquad (1)$$

Chart 1

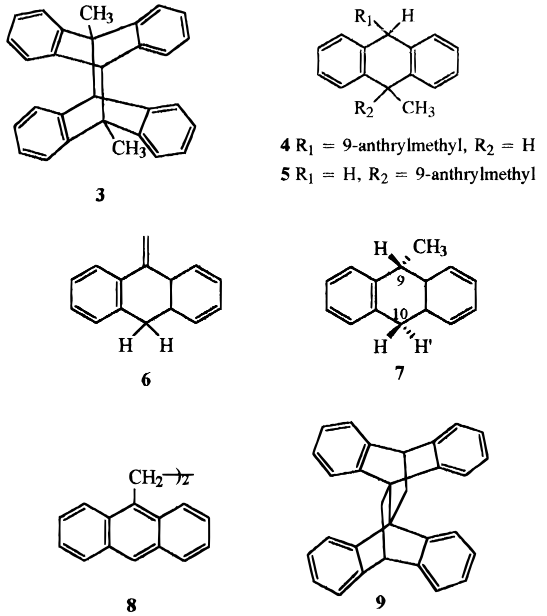

Table 1. Photochemistry of 9-Methylanthracene in the Presence of 1-Ethyl-3-methyl-imidazolium Chloride[a,b]

medium	time (h)	product (%)[c,d]								material balance (%)
		2a	**3**	**4**	**5**	**6**	**7**	**8**	**9**	
molten Salt[e]	3	57.2	21.1	1.0	1.2	t	1.3	t	1.0	>82.8
molten Salt[e]	17	25.8	49.1	1.4	2.4	t	2.2	t	5.8	>86.7
molten Salt[e]	36	18.3	60.4	0.9	1.0	t	2.9	t	10.0	>93.5
1/CH_3CN[f]	3	8.2	76.0	t	t	0.1	0.1	t	0.5	>84.9
1/CH_3CN[f]	17	4.0	79.0	t	t	0.2	0.1	t	0.9	>84.2
1/CH_3CN[f]	36	0.4	83.0	t	t	0.2	0.2	t	0.7	>84.5

[a] Degassed solution photolyzed in a pyrex vessel on a Rayonet reactor at 350 nm. [b] At $t = 0$, 100% **2a**. [c] Yields based on starting **2a**. [d] t = trace amount. [e] 0.065 M **2a** in **1** (55 mol %)/$AlCl_3$. [f] 0.065 M **2a** and 3.41 M **1** in CH_3CN.

Photolysis of 9-CH_3An (**2a**) in deoxygenated CH_3CN yielded the 4 + 4 dimer (**3**) exclusively.[12] Photolysis of 9-CH_3An, on the other hand, in deoxygenated CH_3CN that was 3.41 M in EMIC (**1**) or EMIC (55 mol %)/$AlCl_3$[7,13] afforded **3** (major product) and six other products (**4**−**9**), all of which were synthesized independently.[14] Table 1 summarizes the yields of reactant and products, as well as material balances, as a function of reaction time. Five of the products, **3**,[12] **4**,[15,16] **5**,[15] **8**,[17] and **9**,[17] are dimeric, while two, **6**[15] and **7**,[18] are monomeric. As evidenced by the loss, addition, or movement of hydrogen in **4**−**9**, these hydrocarbons were formed by a series of redox reactions. Furthermore, four of the products, **3**, **4**, **5**, and **6**, have the same oxidation state as 9-CH_3An because they have identical empirical formulas ($C_{15}H_{12}$ or C_5H_4), while **7** is reduced (added H; $C_{15}H_{14}$ versus $C_{15}H_{12}$) and **8** and **9** are oxidized (loss of H; $C_{15}H_{11}$ versus $C_{15}H_{12}$). The photoreactions which are largely bimolecular were faster in the less viscous CH_3CN,[19] and more of the reaction occurred by the 4 + 4 pathway in CH_3CN. Those products that possess the anthracene chromophore were either formed in trace amounts or increased in yield as a function of time and then decayed.

From the above considerations and the fact that several of the photoproducts contain the 9-anthrylmethyl group (**4**, **5**, **6**, **8**, and **9**), it is clear that approximately 1% of the photoreaction in CH_3CN and 20% in EMIC/$AlCl_3$ occurred by pathways initiated by electron transfer from an excited state of 9-CH_3An to EMI^+,[20] with the remaining parts of the reactions yielding the 4 + 4 dimer.

To see why there is a disparity in the behavior in the two solvents, one must consider the free energy of the electron transfer in each case. The free energy of electron transfer from a donor excited state (D*) to a cationic acceptor (A^+) to form

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(8) Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 310.

(9) Hondrogiannis, G.; Lee, C. W.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.* **1993**, *115*, 9828.

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(11) The related toluene radical cation has $pK_a \approx -10$ in CH_3CN[41] and −20 in DMSO (Bordwell, F. G.; Cheng, J.-P. *J. Am Chem. Soc.* **1989**, *111*, 1792).

(12) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976.

(13) The concentrations of **1** and **2a** in CH_3CN were adjusted to correspond to their values in the molten salt.

(14) No products containing the imidazolium ring were found in the product mixture (**3**−**9**) or in the recovered salts (SIMS; ^1H NMR). No chlorinated products were detected either.

(15) Takagi, M.; Harabe, T.; Nojima, M.; Kasabayashi, S. *J. Am. Chem. Soc.* **1983**, *105*, 1311.

(16) Only one of two isomers of **4** (cis; trans) is formed in the photoreactions. Attempts to determine the stereochemistry of the independently made material by X-ray crystallography have so far been unsuccessful (space group *p*21/*a*; thin plates with 16 molecules per unit cell): Alan Hazell, University of Aarhus, unpublished results.

(17) Stewart, F. H. C. *Aust. J. Chem.* **1961**, *14*, 177.

(18) Harvey, R.; Arzadon, L.; Grant, J.; Urberg, K. *J. Am. Chem. Soc.* **1969**, *91*, 4535.

(19) The viscosity of CH_3CN at 25 °C is 0.345 cp (ref 4, p F-41), and that of the molten salt is 32.5 cp.[7b]

(20) For some related cases of methyl-substituted arenes, see: Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290.

Table 2. Free Energy Changes for PET Processes[a]

compound	solvent	E_{00}(S) (kcal/mol)	$E_{1/2}$(OX)[b] (V)	$E_{1/2}$(RED)[b] (V)	$\Delta G(\mathrm{D}^{*1} + \mathrm{A}^{+})$[c] (kcal/mol)
9-MeAn (D)	CH_3CN	74.1	.797	−2.31	
	EMIC/$AlCl_3$	73.0	.692	−1.85	
	BPC/$AlCl_3$	73.0[d]	*e*	*e*	
EMIC (A^+)	CH_3CN			−2.67	+5.8
	EMIC/$AlCl_3$			−2.25[f]	−5.2
BPC (A^+)	CH_3CN			−1.87	−12.6
	BPC/$AlCl_3$			−1.5[f]	

[a] $\Delta G = 23.06[E^0(\mathrm{D^+/D}) - E^0(\mathrm{A/A^-})] - E_{00}(\mathrm{S})$ when the acceptor is ionic. [b] Reference electrodes: Ag/$AgNO_3$(CH_3CN); Al wire in EMIC/$AlCl_3$ (2:1) for EMIC/$AlCl_3$; Al wire in BPC/$AlCl_3$ (2:1) for BPC/$AlCl_3$. [c] D = donor; A = acceptor. [d] Assumed to be identical to value in EMIC/$AlCl_3$. [e] 9-MeAn is not oxidized or reduced within the limits +0.6 to −1.5 V of the molten salt. [f] Cathodic limit.

$D^{+\bullet}$ and $A^{\bullet}$ is given by the Rehm−Weller equation:[21,22] ΔG (kcal/mol) = $23.06[E°(\mathrm{D^{+\bullet}/D}) - E°(\mathrm{A^+/A^\bullet})] - E_{00}$ where the two terms in brackets represent the oxidation and reduction potentials of D and A^+ and E_{00} is the excitation energy of D*. For an electron transfer reaction to be efficient, ΔG should be negative so that the PET is fast and competitive with other photochemical processes such as exciplex formation. As ΔG becomes more endothermic, of course, the rate of electron transfer will decrease and the PET will compete less effectively with other photoreactions. As can be seen in Table 2, the electron transfer from the singlet excited of 9-CH_3An to EMI^+ is exothermic in EMIC/$AlCl_3$, but endothermic in CH_3CN. These data are consistent with the results observed in the two solvents. Furthermore, the Rehm−Weller equation rules out the involvement of the triplet excited state of 9-CH_3An in the electron transfer because anthracenes have singlet−triplet gaps on the order of 30 kcal/mol,[23] thus rendering ΔG for $9\text{-}CH_3An^{*3} + EMI^+ \rightarrow 9\text{-}CH_3An^{+\bullet} + EMI^\bullet$ to be in the range of +25−30 kcal/mol in both solvents. The early part of the photoreaction can thus be summarized:[24]

$$\mathrm{AnCH_3} \xrightarrow{h\nu} \mathrm{AnCH_3}^{*1} \tag{2}$$

$$\mathrm{AnCH_3}^{*1} + \mathrm{AnCH_3} \rightarrow \text{exciplex} \rightarrow 4 + 4 \text{ dimer} \tag{3}$$

$$\mathrm{AnCH_3}^{*1} + \mathrm{EMI}^{+} \rightarrow \mathrm{AnCH_3}^{+\bullet} + \mathrm{EMI}^{\bullet} \tag{4}$$

$$\mathrm{AnCH_3}^{+\bullet} + \mathrm{Cl}^{-} \rightarrow \mathrm{AnCH_2}^{\bullet} + \mathrm{HCl} \tag{1}$$

To see where the added hydrogens in **7** and the repositioned hydrogens in **4**, **5**, and **6** came from, three deuterium-labeling experiments were carried out in the basic molten salt.[25] In the first, 9-CD_3An (**2b**), prepared by the reaction of CD_3MgI with anthrone,[26] was photolyzed in EMIC/$AlCl_3$, and the relevant products were analyzed for H/D content. In the second, 9-CH_3An was photolyzed in 2-deuterioEMIC[27] /$AlCl_3$, and in the third, 9-CH_3An was photolyzed in 2,4,5-trideuterioEMIC[27]/$AlCl_3$. Because the results of experiment 3 were no different than those obtained in experiment 2, it is clear that the hydrogens at C-4 and C-5 of EMIC are not involved in the photochemistry. Experiment 3 will not be discussed further.

Table 3. Deuterium Content of **6**

system	% deuterium d_0	d_1	d_2	d_3	d_4
9-CH_3An/EMIC-d_1	64	34	2		
9-CD_3An/EMIC			72	26	2

Table 4. Deuterium Content of **7**

system	% deuterium at position[a] 9	10	10′
9-CH_3An/EMIC-d_1	19	37	21
9-CD_3An/EMIC	30	42	7

[a] %D = [D/D + H] × 100 at each position.

Formally, **6** is formed by transfer of a hydrogen from the methyl group of 9-CH_3An to C-10. If concerted, this reaction corresponds to a 1,5-sigmatropic shift. The results of experiments 1 and 2 rule out this possibility, however. The deuterium content of **6**, which was determined on samples isolated after 17 h of photolysis by GC/MS using the molecular ion, is summarized in Table 3.[28] 9-CH_3An/EMIC-d_1 yielded **6** with both D (34%) and H (66%) at C-10, while 9-CD_3An/EMIC yielded **6** again with D (26%) and H (72%) at C-10. Thus, the H/D, which is lost from the methyl group of the substrate, returns to C-10 part of the time, likely in the form of HCl/DCl, and the H/D attached to C-2 of EMIC returns the other. Thus, the repositioned hydrogen in **6** came from two sources.

Reduction product **7** is formed by adding two hydrogens to **2**. If one can add hydrogen or deuterium, however, as is possible in the deuterium-labeling experiments, six analogues of **7** can be formed: A (d_0), B (9-*d*), C (10-*d*), D (10′-*d*), E (9,10-d_2), and F (9,10′-d_2). In principle, it is possible to determine the contribution of all six species using a combination of ^{1}H[29] and ^{2}H NMR spectroscopies and MS. Unfortunately, the ^{2}H NMR spectrum of **7** was not sufficiently resolved to make this possible.[30] Nonetheless, the ^{1}H NMR and mass spectra of **7** isolated after 17 h of irradiation provided a wealth of information, some of which is shown in Table 4. See the Experimental Section for other data. Inspection of these data shows that, as with **6**, the added hydrogen in **7** at positions 9, 10, and 10′ arose from the methyl group of the substrate and H/D attached to C-2 of EMIC.

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[21] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[22] If D and A are uncharged, there will also be a Coulombic term, $-e^2/d\epsilon$, where *e* is the charge of the electron, *d* is the distance between $D^{+\bullet}$ and $A^{-\bullet}$ and ϵ is the dielectric constant of the solvent.

[23] 9-CH_3An has a singlet energy of 74.1 kcal/mol in CH_3CN and 73.0 kcal/mol in basic EMIC/$AlCl_3$. Its triplet energy probably lies in the range of 40−42 kcal/mol. See: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

[24] Attempts were made to study the early parts of these reactions by flash photolysis. Unfortunately, the yields of relevant transients were too low in acetonitrile. In both media, multiphoton ionization was a problem. J. Wirz, University of Basel, unpublished results.

[25] These were not carried out in CH_3CN because of the low yields of the relevant photoproducts.

[26] Tanko, J. M.; Mas, R. H. *J. Org. Chem.* **1990**, *55*, 5145.

[27] Dieter, K. M.; Chester, J. D., Jr., Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722.

[28] Because **6** should not contain d_2 and d_4 when generated from **2a** and **2b**, respectively, the 2% that was obtained for d_2 and d_4 can be taken as the error limits of the measurements.

[29] The ^{1}H NMR assignments for **7** are found in Brinkmann, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Stothers, J. B.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5912.

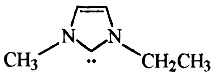
[30] The ^{2}H NMR spectrum clearly showed the presence of deuterum at positions 9, 10, and 10′ from **7** isolated from both experiments.

Determining the deuterium content of **4** and **5** proved more troublesome because of small sample sizes which made NMR analysis problematical and the MS lacked suitable fragmentation patterns.[31] Nonetheless, by comparing the mass spectra of authentic **4** and **5** with the same compounds isolated from the two deuterium-labeling experiments, it is clear that hydrogen and deuterium have been added to the hydrocarbons in both experiments.

It is now appropriate to provide mechanisms by which products **4**−**9** arose. Clearly **8** and **9** are formed by coupling of two 9-AnCH$_2^\bullet$, head-to-head to form **8** and head-to-tail followed by intramolecular Diels−Alder reaction to form **9** (eq 5). Formation of **4**−**7**, however, is more complex because each of them, as indicated by the deuterium-labeling experiments, requires the use of HCl and EMI$^+$.

$$2(9\text{-AnCH}_2^{\bullet}) \rightarrow \mathbf{8} + \mathbf{9} \tag{5}$$

Compound **6** is formed by adding a hydrogen atom to 9-AnCH$_2^\bullet$, but not by hydrogen atom abstraction from HCl, which is endothermic by 18 kcal/mol,[32] or from EMI$^\bullet$, which is exothermic.[33,39] Instead the hydrogen is transferred in a two-step process, first involving electron transfer from EMI$^\bullet$ to AnCH$_2^\bullet$, an exothermic reaction,[33] to form EMI$^+$ and AnCH$_2^-$ and then proton transfer from HCl and EMI$^+$ to AnCH$_2^-$ [40] to form **6**,[44] chloride, and a nucleophilic carbene EMI:.[45] This is confirmed by the following observations. (1) Photolysis of 9-chloromethylanthracene (9-ClCH$_2$An) in the basic melt yielded **8**, **9**, and **2a**, but no **6**. Thus, when 9-AnCH$_2^\bullet$ is generated under conditions where it cannot yield 9-AnCH$_2^-$, it abstracts a hydrogen atom (source unknown) to form **2a**, but not **6**. (2) Likewise, reduction of 9-ClCH$_2$An with Bu$_3$SnH/AIBN, a reaction also going through 9-AnCH$_2^\bullet$, afforded **2a** quantitatively. (3) On the other hand, 9-AnCH$_2^-$ behaves differently. Rigaudy et al.[48] have shown that 9-AnCH$_2^-$ abstracts protons from *tert*-butyl alcohol at both CH$_2$ to form **2a** and C-10 to form **6**. Thus, **6** is formed by the following pathway.



10 (EMI:)

$$9\text{-AnCH}_2^{\bullet} + \text{EMI}^{\bullet} \rightarrow 9\text{-AnCH}_2^{-} + \text{EMI}^{+} \tag{6}$$

$$9\text{-AnCH}_2^{-} + \text{HCl} \rightarrow \mathbf{6} + \text{Cl}^{-} \tag{7}$$

$$9\text{-AnCH}_2^{-} + \text{EMI}^{+} \rightarrow \mathbf{6} + \text{EMI:} \tag{8}$$

$$\text{EMI:} + \text{HCl} \rightarrow \text{EMIC} \tag{9}$$

Compounds **4** and **5** are also generated in multistep reactions starting with 9-AnCH$_2^\bullet$. First, the radical 9-AnCH$_2^\bullet$ attacks 9-CH$_3$An at positions 9 and 10, respectively, to form new carbon-centered radicals,[49] each of which formally abstracts a hydrogen atom to give the products. Because these H atom transfer reactions have many of the same characteristics as that associated with the formation of **6**, it is more likely that the carbon-centered radicals are reduced to carbanions by electron-transfer from EMI$^\bullet$ which is followed by the abstraction of protons from HCl and EMI$^+$. These two-step H atom transfers are lent further credence by the results of experiments described below.

The formation of the reduction product is most unusual in that it arose from the radical anion of **2a** (9-CH$_3$An$^{-\bullet}$) in a Birch-like reduction.[50] Several lines of evidence confirm this. Firstly, electrons became available, in the form of EMI$^\bullet$, when 9-AnCH$_2^\bullet$ and thus **8** and **9** were formed. Secondly, the 9-CH$_3$An + EMI$^\bullet$ → 9-CH$_3$An$^{-\bullet}$ + EMI$^+$ is exothermic in both CH$_3$CN (ΔG= −8.3 kcal/mol) and the molten salt (ΔG= −9.2 kcal/mol) (Table 2).[51] Thirdly, metal (Li/liquid NH$_3$) and electrochemical (bulk electrolysis in the molten salt) reduction, both of which yield 9-CH$_3$An$^{-\bullet}$, gave **7** exclusively. Lastly, as described in the next two paragraphs, when the energetics of the electron transfer reaction forming 9-CH$_3$An$^{-\bullet}$ becomes unfavorable, no **7** was formed.

$$9\text{-CH}_3\text{An} + \text{EMI}^{\bullet} \rightarrow 9\text{-CH}_3\text{An}^{-\bullet} + \text{EMI}^{+} \tag{10}$$

$$9\text{-CH}_3\text{An}^{-\bullet} \xrightarrow{+\text{H}^+,\ +\text{e},\ +\text{H}^+} \mathbf{7} \tag{11}$$

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(31) For example, the molecular ions were flanked by significant M−H and M−2H peaks.

(32) The bond dissociation energy of HCl is 103 kcal/mol, and that of 9-CH$_3$An is 85 kcal/mol (calculated value: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(33) Based on the pK_a of 9-CH$_3$An (31.1)[34] and an imidazolium ion structurally related to EMI$^+$(24)[35] in DMSO, ΔG = −9.7 kcal/mol for AnCH$_2^-$ + EMI$^+$ → AnCH$_3$ + EMI: (carbene) at ambient temperature. **6** is less stable than 9-CH$_3$An by ΔG = 6.1 kcal/mol in the gas phase.[36] If one neglects differences in the free energies of solution of **6** and 9-CH$_3$An, ΔG = −3.6 kcal/mol for AnCH$_2^-$ + EMI$^+$ → **6** + EMI:. In order to calculate ΔG for AnCH$_2^\bullet$ + EMI$^\bullet$ → **6** + EMI:, ΔG for AnCH$_2^\bullet$ + EMI$^\bullet$ → AnCH$_2^-$ + EMI$^+$ is also needed. Intuitively, one would expect this reaction to be quite exothermic because an electron is being added to a nonbonding MO and an aromatic species is created on loss of an electron. This is confirmed from the reduction potential of EMI$^+$ (−1.7 V in CH$_3$CN on Pt versus Ag/AgClO$_4$)[37] and the oxidation potential of 9-AnCH$_2^-$ (−0.62 V in DMSO on Pt versus Ag/AgI).[38] Even considering the obvious differences in the two electrochemical experiments, $\Delta G \approx -20$ kcal/mol for AnCH$_2^\bullet$ + EMI$^\bullet$ → AnCH$_2^-$ + EMI$^+$. Thus, the hydrogen atom abstraction reaction, AnCH$_2^\bullet$ + EMI$^\bullet$ → **6** + EMI:, is exothermic ($\Delta G \approx$ −3.6−20 kcal/mol).

(34) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(35) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267.

(36) Bartmess, J. E.; Griffith, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 2931.

(37) Gilfford, P. R.; Palmisano, J. B. *J. Electrochem. Soc., Electrochem. Sci. Tech.* **1987**, *134*, 610.

(38) Bausch, M. J.; Guadalupe-Fasano, C.; Peterson, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 8384.

(39) Other hydrogen atom abstractions are possible but less likely (endothermicity of reaction; lack of formation of appropriate products).

(40) Both proton transfers are exothermic: pK_a(HCl) = 8.9 in CH$_3$CN[41] and 2.1 in DMSO,[42] while pK_a(**6**) ≈ 27 in DMSO based on the pK_a of 9-CH$_3$An[34] and the energy difference of **6** and **1a**.[36] pK_a (1,3-diisopropyl-4,5-imidazolium ion) = 24 in DMSO.[35] Other imidazolum ions have pK_as around 20.[43]

(41) Value cited in Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(42) Cooke, C.; McCallum, C.; Pethybridge, A. D.; Prue, J. E. *Electrochim. Acta* **1975**, *20*, 591.

(43) Elridge, J. A.; Jones, J. R.; O'Brien, C.; Evans, E. A.; Sheppard, H. C. *Adv. Heterocyclic. Chem.* **1970**, *16*, 1.

(44) 9-CH$_3$An could also be regenerated by proton and/or hydrogen atom abstraction reactions. We have no evidence for this. Analysis of recovered 9-methylanthracene in the deuterium-labeling experiments revealed no mixing of H and D at the methyl position.

(45) Carbenes similar in structure to EMI: have been synthesized and isolated.[46] Attempts to prepare EMI: have, unfortunately, failed. In any event, EMI: would not survive the reaction conditions because HCl generated in the photoreaction would react readily with it to form EMIC.[47]

(46) Arduengo, A. J., III; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(47) Recovered EMIC in the deuterium-labeling experiments thus should contain both H and D at C-2. Unfortunately, this was not detected. This is not surprising, however, owing to the preponderance of EMIC/EMIC-d_1 in the initial solutions (EMIC-d_1: **1a** ≈ 50, for example).

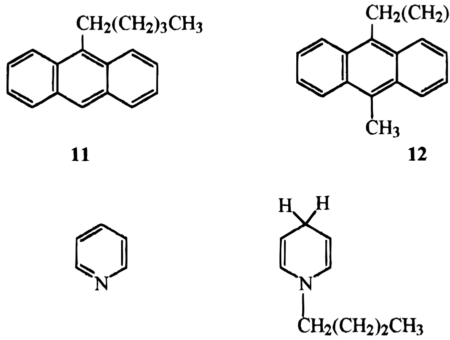
(48) Rigaudy, J.; Seuleiman, A. M.; Cuong, N. K. *Tetrahedron* **1982**, *38*, 3143.

(49) Both additions are exothermic (Benson's method: citation in ref 32).

(50) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, 1972; Chapter 3.

(51) These ΔGs do not include a small Coulombic term due to the attraction of CH$_3$An$^{-\bullet}$ and EMI$^+$.

Chart 2



11 **12** **13** **14**

Table 5. Photochemistry of 9-Methylanthracene in the Presence of *N*-Butylpyridium Chloride[a,b]

medium	time (h)	products (%)[c] 2a	3	8	9	others	material balance (%)
molten salt[e]	17	64.6	2.3	1.8	6.9	Yes[d]	>75.6
CH_3CN[f]	17	1.0	3.3	3.5	14.9	Yes[d]	>22.7

[a] Degassed solution photolyzed in a pyrex vessel in a Rayonet reactor at 350 nm. [b] At $t = 0$, 100% **2a**. [c] Yields based on starting **2a**. [d] Products **11**−**14** plus two unidentified products; yields not determined. [e] 0.78 M **2a** in BPC (55 mol %)/AlCl). [f] 0.078 **2a** + 1.2 M BPC in CH_3CN.

N-Butylpyridinium chloride (BPC) is much more easily reduced than EMCI, is soluble in CH_3CN, and forms a basic room temperature molten salt with $AlCl_3$.[52] Unlike EMIC, however, BPC is a weaker Brϕnsted acid. Because of the ca. 0.8 V difference in reduction potentials of EMIC and BPC, the reduced form of BP^+ ($BP^\bullet$) is a much poorer reducing agent than $EMI^\bullet$. In fact, the reaction required to initiate the formation of **7** in BPC/CH_3CN, 9-CH_3An + $BP^\bullet$ → 9-$CH_3An^{-\bullet}$ + BP^+, is endothermic by 10.1 kcal/mol.[53] Thus, BP^+ is a better oxidizing agent than EMI^+, which should facilitate the initial PET, but $BP^\bullet$ is a poorer reductant than $EMI^\bullet$, which should suppress the formation of **7**.

Photolysis of 9-CH_3An in BPC/CH_3CN and the molten salt BPC (55 mol %)/$AlCl_3$ yielded **3**, **8**, and **9**, but no **7**, **4**, **5**, or **6**, and several new products, 9-pentylanthracene (**11**), 9-butyl-10-methylanthracene (**12**), pyridine (**13**), and *N*-butyl-1,4-dihydropyridine (**14**), and two unidentified compounds, both of which contain 9-methylanthracene and pyridine or *N*-butylpyridine moieties (Table 5). The photoreaction was considerably faster in the less viscous CH_3CN, and as expected, the fraction of the reaction yielding the 4 + 4 dimer is greatly diminished in both solvents. The material balance is fairly good in the molten salt but rather poor in CH_3CN, which can be attributed in part to the formation of the new products, none of which was quantitated in these experiments.[54]

Although the formation of **8** and **9**, as well as **11**−**14**, is interesting in that it requires 9-$AnCH_2^\bullet$ and/or $BP^\bullet$,[55] the lack of **7** is most telling because it points to the formation of 9-$CH_3An^{-\bullet}$ in the EMIC-containing media. The lack of **4**−**6** in the BPC-containing solvents is also telling. As the formation of each of them in the presence of EMIC required the conversion of a radical into an anion by electron transfer (followed by protonation), it is conceivable that each of these reductions is also endothermic in the BPC-containing solvents.

$$\text{9-}CH_3An^{*1} + BP^+ \rightarrow \text{9-}CH_3An^{+\bullet} + BP^\bullet \qquad (12)$$

$$\text{9-}AnCH_2An^{+\bullet} + Cl^- \rightarrow \text{9-}AnCH_2^\bullet + HCl \qquad (13)$$

$$\text{9-}AnCH_2^\bullet + BP^\bullet \rightarrow \mathbf{11} + \mathbf{12} + \mathbf{13} \qquad (14)$$

$$\text{9-}CH_3An + BP^\bullet \not\rightarrow \text{9-}CH_3An^{-\bullet} + BP^+ \qquad (15)$$

Although it is possible to generate radical cations and radical anions of the same species together in solution electrochemically[56] and on solids, which possess different oxidizing and reducing domains, photochemically,[57] the formation of 9-$CH_3An^{+\bullet}$ and 9-$CH_3An^{-\bullet}$ during the photochemistry of 9-CH_3An/EMIC represents the first photochemical example of the phenomenon in fluid solution.[58,59] Although this phenomenon may never be common, e.g. 9-CH_3An + BPC and alkylbenzenes + *N*-methylacridinium ion do not show it,[60] it still should be detectable in a large number of cases when the following criteria are fulfilled. (1) The donor and acceptor must have appropriate oxidation potentials such that $D^* + A \rightarrow D^{+\bullet} + A^{-\bullet}$ and $D + A^{-\bullet} \rightarrow D^{-\bullet} + A$ are exothermic. (2) The donor radical cation should have a facile chemical outlet such as deprotonation which inhibits an energy-wasting return to D and A. (3) $A^{-\bullet}$ must be sufficiently long lived so that it can find and reduce D.

Experimental Section

Methods, Chemicals, and Instruments. 1-Ethyl-3-methylimidazolium chloride (**1**) and $AlCl_3$ were prepared and purified as described elsewhere.[61] *N*-Butylpyridinium chloride was prepared by the method of Robinson and Osteryoung.[52] 9-Methylanthracene (Aldrich) (**2a**) was recrystallized once from ethanol. 9-Chloromethylanthracene was used as received (Aldrich). Molten salts and solutions of 9-methylanthracene in the molten salts were prepared in a nitrogen atmosphere glove box and manipulated by Shlenk line techniques. Photolysis was carried out in vacuum-sealed Pyrex glass tubes in a Rayonet Type RS Photochemical Reactor using 3500 Å lamps. Reaction mixtures were quenched in ice water. After the aqueous phase was neutralized by 6 M sodium hydroxide, the organic products were extracted into methylene chloride. Products were isolated by column chromatography on silica gel (petroleum ether) and prep HPLC on a Varian model 5000 HPLC, which had a programmable gradient elution capability, a variable UV wavelength detector, and a Varian 4400 integrator. A Whatman Partisil 10 ODS-3 column was used for product separation (98% CH_3CN/H_2O). Product yields and ratios were determined by a combination of ^1H NMR spectroscopy (Brucker 250 and 400 MHz instruments), GC/MS (Hewlett-Packard 5890 gas chromatograph and 5970 series mass selective analyzer, with a crossbonded 100% dimethyl polsiloxane column), using internal standards where appropriate, and

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(52) Robinson, J.; Osteryoung, R. *J. Am. Chem. Soc.* **1979**, *101*, 323.

(53) (a) This ignores the small Coulombic term. (b) Because 9-CH_3An is not reduced within the BPC/$AlCl_3$ window, ΔG for the molten salt reaction is unavailable but should have a value similar to that in CH_3CN.

(54) Because the photoreactions in BPC are redox in nature, reduction products such as *N*-butyl-1,4-dihydropyridine and the BP dimer must be formed in the reaction. The dimer may have gone undetected because of its reaction with HCl generated in the reaction to form a salt.

(55) The formation of **11**, **12**, and **13**, for example, requires a transfer of a butyl group from $BP^\bullet$ to 9-$AnCH_2^\bullet$, either concertedly or stepwise.

(56) Faulkner, L. R.; Glass, R. S. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic: New York, 1982; p 191.

(57) See, for example: Liu, X.; Iu, K.-K.; Thomas, J. K. *Chem. Phys. Lett.* **1993**, *204*, 163.

(58) The photochemistry of An in EMIC (45 mol %)/$AlCl_3$ is initiated by electron transfer for An^{*1} to protonated An, formed by reaction of HCl with An.[9] Thus An is the donor and indirectly the acceptor.

(59) (a) The reaction of An^{*1} + An → exciplex → $An^{+\bullet}$ + $An^{-\bullet}$ is exothermic in CH_3CN, but the exciplex collapses to the 4 + 4 dimer instead. See: Vauthey, E.; Hasselbach, E.; Suppan, P. *Helv. Chim. Acta* **1987**, *70*, 347. (b) The issue of whether the reaction 9-$CH_3An^{+\bullet}$ + 9-$CH_3An^{-\bullet}$ → 4 + 4 dimer occurs is unanswered. Such dimerizations are known in electrochemical systems.[56]

(60) Fujita, M.; Ishida, A.; Majima, T.; Fukuzumi, S.; Takamuka, S. *Chem. Lett.* **1995**, 111.

(61) Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 525, 5075 and references cited therein.

by weight. EMIC-d_1 (4% H at C-2),[27] EMIC-d_3 (4−5% H at C-2, C-4, and C-5),[27] and 9-methylanthracene-d_3 (**2b**)[26] (5% H at methyl) were prepared by literature methods.

Characterization of Products. All the photoproducts isolated from the EMIC-containing solutions were identical to authentic materials. The 9-methylanthracene photodimer (**3**) was prepared by photolysis of **2a** in deoxygenated CH_3CN. 9-(9-Anthylmethyl)-10-methyl-9,10-dihydroanthracene (**4**),[15] 9-(9-anthrylmethyl)-9-methyl-9,10-dihydroanthracene (**5**),[15] 9-methylene-9,10-dihydroanthracene (**6**),[15] 9-methyl-9,10-dihydroanthracene (**7**),[18] 1,2-bis(9′-anthryl)ethane (**8**),[17] and lepidopterene (**9**)[19] were prepared by literature methods.

The new products formed in the BPC-containing media were characterized by GC/MS. As the purpose of photolyzing **2a** in the BPC-containing media was to see if **7** were formed there, none of the new compounds were synthesized independently or quantitated.

Deuterium Analyses. Compound 6. The deuterium content was determined by mass spectrometry using the molecular ion. See Table 3 for the results.

Compound 7. There are six mono- and dideuterio-analogs of **7** which can be produced in the photoreaction: no *d* (A), 9-*d* (B), 10-*d* (C), 10′-*d* (D), 9,10-d_2 (E), and 9,10′-d_2 (F). By a combination of MS and ^{1}H and ^{2}H NMR spectroscopy, it is possible in principle to deduce the contribution of all six components. Unfortunately, the proton-decoupled ^{2}H NMR spectra, obtained in an unlocked mode, were not well enough resolved to be useful. Thus, less than the maximum information content was obtained. For MS, the $M - CH_3$ peak was used. The ^{1}H resonances were assigned on the basis of the work of Brinkmann et al.[29] See Table 4 for pertinent results. Additional results were as follows: (1) For photolysis of **2a** in the monodeuterated molten salt for 17 h, A = 33%, B = 9%, C + D = 48%, E + F = 10%, C + E = 37%, and D + F = 21%. The order of abundance of the six species is A > C > D > B > E, F. The total deuterium content at each position is 9, 19%; 10, 37%; 10′, 21%. (2) For photolysis of **2b** in the nondeuterated molten salt for 17 h, A = 35%, B = 16%, C + D = 35%, E +F = 14%; C + E = 42%, and D + F = 7%. The order of abundance of the six species is A ≥ C > B > E > F, D. The total deuterium content at each position is 9, 30%; 10, 42%; 10′, 7%.

Compounds 4 and 5. Because the compounds are only formed in trace amounts in CH_3CN, only the reaction of **2a** in the monodeuterated molten salt for 17 h was analyzed. Because the compounds are air sensitive and difficult to separate, the analysis was carried out by MS on a mixture of the two compounds. It was not possible to quantitate the deuterium content because the fragmentation pattern of each compound was not appropriate for such an analysis. Nonetheless, by comparing the MS of nondeuterated **4** and **5** to the test sample, it is apparent that **4** and **5** contain deuterium at C-9 and C-10.

For the reaction of **2a** in the trideuterated molten salt, the products had a deuterium distribution similar to that for reactions run in the monodeuterated molten salt. Recovered **2a** and **2b** from the photolyses showed little deuterium incorporation and loss, respectively, after photolysis in the appropriate molten salts.

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