Chemistry of Arylalkyl Radical Cations: Deprotonation vs Nucleophilic Attack

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Radical-cation-mediated oxidation of 9-methylanthracene (9MA) by pyridine/iodine in chloroform produces mainly the product of nucleophilic attack at the open C-10 position. When methyl is replaced by ethyl as in 9-ethylanthracene (9EA), the nucleophilic product is the only one observed. Alternatively, aceanthrene (AA), the 1,9-ethano-bridged equivalent of 9EA, produces mainly the product of side-chain substitution. Stereoelectronic control in the deprotonation is proposed as the rationale for this difference in reactivity, as well as for other radical-cation-mediated oxidations.

Introduction

Arylalkyl radical cations can partition along two mechanistically related channels. One involves proton loss, leading to side-chain oxidation, and the other involves nucleophilic attack, leading to ring oxidation. The rate of proton loss, the kinetic acidity, is apparently the key branch point between these two pathways and has been implicated in biooxidation pathways leading to carcinogenesis,[1] although not, apparently, in P450-mediated oxidations.[2]

Methylarene radical cations are recognized to be very strong acids thermodynamically by those familiar with the work of Weller,[3] Arnold,[4] and Bordwell.[5] Arnold's contribution was to recognize that the pK_as of toluene radical cation (−12)[4] and 9,10-dimethylanthracene (−6)[5b,6] can be calculated by use of the thermodynamic cycle represented by eq 1. Thus a strong thermodynamic driving force exists for rapid proton loss once the radical cation is formed, leading ultimately to the product of solvolysis. In this regard, alkylanthracenes and higher condensed aromatics represent groups distinct from the monoalkylbenzenes, for which hydrogen atom transfer dominates,[2a,7] and from alkylamines, whose acidities are too low for facile deprotonation.[8]

$$\mathrm{p}K_a(\mathrm{ArCH_3}^{\bullet+}) = \mathrm{p}K_a(\mathrm{ArCH_3}) - [E_{ox}(\mathrm{ArCH_3}) - E_{ox}(\mathrm{ArCH_2}^{\bullet})]/2.3RT \quad (1)$$

Given the high thermodynamic acidity of radical cations, one might question why this is not the exclusive pathway for one-electron oxidations. The answer is that deprotonation may involve significant entropic and enthalpic barriers. In some cases, for instance, proton transfer may even occur from the weaker thermodynamic acid.[9] Thus proton transfer reactions may be inhibited by a number of factors. In nonaqueous solvents such reactions are known to be slow despite favorable thermodynamics, especially when carbon acids are involved.[10] For instance, proton loss from toluene radical cation is estimated to be 4 orders of magnitude slower in acetonitrile than in water.[11] For the radical cation of dimethylbenzylamine, proton loss occurs faster from the methyl group despite thermodynamically favored loss from the benzyl group, an effect attributed to unfavorable steric interactions in the latter.[12] For hydrocarbon ions and radicals where stabilization is strictly governed by p-orbital overlap, the inability of the newly forming carbon free valence to achieve overlap with the π-orbital framework of the aromatic ring may prevent facile proton loss. The idea of a stereoelectronic effect was given support by the observation that deprotonation of *p*-cymene (*p*-isopropyltoluene) radical cation occurs from the methyl group, not the isopropyl group.[13] This effect was attributed to the bisected conformation expected for the neutral, preventing the isopropyl group from achieving the requisite planarity. More recently, Baciocchi has pointed out that this hydrocarbon adopts a planar conformation in its radical cation state and has ascribed this result to steric hindrance to approach by base rather than to a stereoelectronic effect.[13] Indeed, in studies which space does not permit us to elaborate, we have discovered that this stereochemistry is solvent dependent, with increasing water concentration favoring deprotonation of the sterically more encumbered isopropyl group.[14]

In order to examine stereoelectronic effects in the absence of these conformational ambiguities, we have employed 9-alkylanthracenes. Previously we have shown

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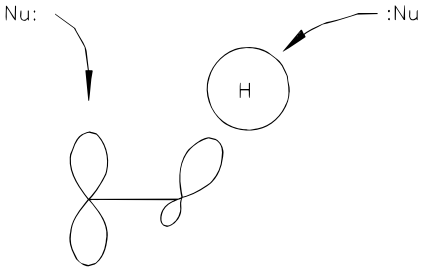

Figure 1. Nucleophilic attack vs deprotonation.

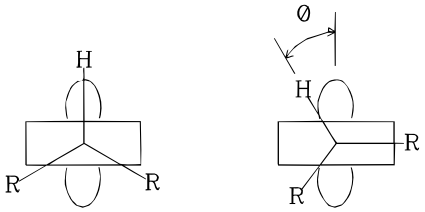

Figure 2. In-plane vs out-of-plane conformations.

that 9-alkylanthracenes undergo efficient pyridination under oxidative conditions with regiochemistry dependent upon the relative rate of C−H bond cleavage.[15] Our primary goal here is to assess the degree to which efficient deprotonation requires that the dihedral angle of the CH bond with the molecular plane be close to 90° (see Figure 2). ESR studies of 9,10-diethylanthracene and 6-ethylbenzo[*a*]pyrene radical cations yield a hyperfine coupling constant indicative of a ca. 90° alignment of the ethyl group with respect to the aromatic plane,[16] which would make deprotonation difficult in the presence of a compelling stereoelectronic effect. Indeed, we have discovered that 9,10-diethylanthracene undergoes inefficient side-chain oxidation with tris(phenanthroline)iron(III) in aqueous acetonitrile, a phenomenon we associated with steric inhibition of deprotonation.[17] Moreover, the oxidation potentials of anthracene derivatives are low enough to be accessible to weak oxidants and are better models for the biooxidation of polynuclear aromatic hydrocarbons.

Even in the absence of strong steric constraints, proton transfer may not dominate the radical cation decay in anthracene derivatives. The reason is that a competing process, nucleophilic attack at the *meso* position, may occur (see Figure 1). Pross has suggested that such nucleophilic attack on radical cations is inhibited by orbital symmetry considerations.[10b] In contrast to this prediction, Parker has observed that nucleophilic attack by pyridine on phenylanthracene radical cations occurs extremely rapidly.[18] Similarly, we have discovered that 9-methylanthracene undergoes iodine-mediated reaction with pyridine to yield the product of ring oxidation as the major product rather than side-chain oxidation, despite the presence of a C−H bond collinear with the π-system.[15] We have also observed that this stereoselectivity may be reversed by use of a trimethylsilyl group as a latent proton. In order to obtain a clearer understanding of the role of such stereoelectronic effects, we elected to oxidize anthracenes in which a substituent at the 9-position tested the effect of various steric constraints. The symmetrically equivalent 10-position was left unsubstituted, in which case nucleophilic attack followed by deprotonation could occur. For the 9-substituted anthracenes, in addition to the control substrate 9-methylanthracene (9MA), we chose the stereochemically unambiguous 9-ethylanthracene (9EA) and its constrained equivalent, 1,9-ethanoanthracene, i.e., aceanthrene (AA). While 9-ethylanthracene is forced to adopt a perpendicular conformation, aceanthrene is forced to adopt a conformation in which the C−H bond is nearly collinear with the π-system. The competing nucleophilic attack on the open *meso* position provides a molecular "clock", allowing us to compare reactivities within the same family by considering the ratio of side-chain to ring oxidation. Because of the difficulties associated with secondary oxidation, particularly in aqueous media, we have found that I_2/pyridine oxidations are the most convenient for investigating the primary products of radical-cation-mediated oxidation. The pyridinium salts resulting from the initial deprotonation or nucleophilic attack are resistant to further oxidation, can be isolated as crystalline salts, and yield to straightforward spectroscopic or X-ray structure determination. Thus the relative yields of products resulting from pyridination provide a reliable indicator of the ratio of primary radical cation reactivity.

Results

Synthesis. Aceanthrene was prepared by Wolff−Kischner reduction of aceanthrone, which was synthesized by the method of Scott.[19] This procedure proved to be more accessible than the synthesis of Plummer.[20] Ethylanthracene was conveniently prepared by nickel-catalyzed coupling[21] of 9-bromoanthracene and ethylmagnesium chloride.

Oxidation. Oxidation of each 9-alkylanthracene with either iodine or Ce(IV) in chloroform led cleanly to products of side-chain and ring oxidation. The products were readily isolated by precipitation with ether and identified on the basis of their nuclear magnetic resonance spectra by analogy with the products of 9MA oxidation previously synthesized and subjected to single-crystal X-ray diffractometry.[15] Thus the nucleophilic products, (10-alkylanthracenyl)pyridinium salts, were characterized by a two-proton doublet at δ 9.46, a one-proton triplet at δ 9.08, and a two-proton triplet at δ 8.65 for the pyridinium group and the loss of the *meso* proton resonance at δ 8.97. The side-chain-substituted pyridinium salts were characterized by a two-proton doublet at δ 8.97, a one-proton triplet at δ 8.63, and a two-proton triplet at δ 8.11 for the pyridinium group, in addition to the loss of the α-alkyl proton resonances at ca. δ 3.65. In the case of AA, the side-chain oxidation product was characterized by three doublets of doublets at δ 3.86, δ 4.47, and δ 7.52. In addition, fractional crystallization

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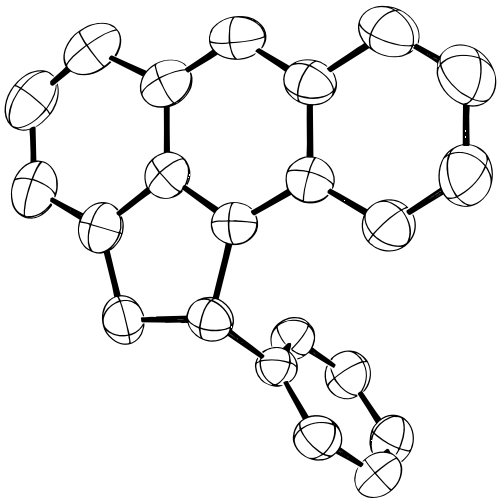
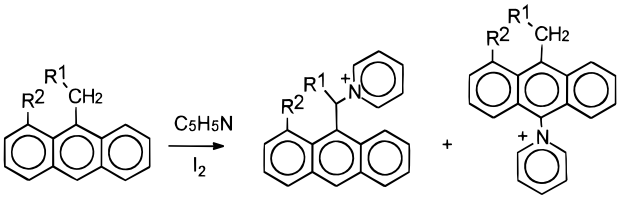


Figure 3. Crystal structure of 4-aceanthrylpyridinium (4AAP) perchlorate.



9MA, $R^1 = R^2 = H$	**AMP**	10:90	**MAP**
9EA, $R^1 = Me$, $R^2 = H$	**EAP**	0:100	**AEP**
AA, $R^1 + R^2 = -CH_2-$	**9AAP**	76:24	**4AAP**
9TMSMA, $R^1 = Me_3Si$, $R^2 = H$	**AMP**	84:16	**MAP**

Figure 4. Pyridine/iodine oxidation of dialkylanthracenes.

allowed recovery of pure material which was subjected to single-crystal X-ray diffractometry, which confirmed the proposed structure (see Figure 3).

The ratios of side-chain to ring-substituted product were extremely sensitive to the identity of the alkyl group. In the case of the methyl substituent, 9MA, the ratio was dominated by the nucleophilic product *N*-(10-methylanthracen-9-yl)pyridinium iodide (MAP), as reported, in addition to the minor product *N*-(9-anthracenylmethyl)pyridinium iodide (AMP) (see Figure 4).[15] No side-chain oxidation to produce *N*-[(9-anthryl)-1-ethyl]-pyridinium iodide (AEP) was observed with 9EA; rather, the single product of nucleophilic substitution at the 10-position was observed, namely, *N*-[(10-ethyl-9-anthryl)-1-ethyl]pyridinium iodide (EAP) (see Figure 4). However, when methyl is replaced with a 1,9-ethano group in AA, the selectivity is reversed, producing a ratio of the side-chain product *N*-(9-aceanthryl)pyridinium iodide (9AAP) to ring-oxidized product *N*-(4-aceanthryl)pyridinium iodide (4AAP) of 76:24. The structure of the major product 9AAP was confirmed by single-crystal X-ray determination (see Figure 3).

Discussion

The dramatic difference in reactivity among 9MA, AA, and 9EA suggests that the stereoelectronic effect must be more compelling than we realized. Assuming that nucleophilic attack at C-10 of the AA and 9MA radical cations occurs at comparable rates, the ratio of deprotonation for the two substrates, i.e., of the ethano group vs the methyl group, is 28:1. Since we detect no oxidation of the ethyl group, we cannot provide a reliable ratio for the perpendicular ethyl to planar "ethyl", ie., ethano, groups. However, on the basis of reasonable limits of detection, we estimate a relative rate of >1000:1. Thus while the methylanthracene 9MA always presents a C-H group perpendicular to the molecular plane, oxidation of the ethano group, for which disposition of the C-H moieties is 30° from vertical, takes place with greater facility. Conversely, rotation of the ethyl group by 30° could allow similar disposition of the breaking CH group within 30° of perpendicular, yet oxidation of the ethyl group occurs only under forcing conditions.[22]

Several factors contributing to this strong stereoelectronic effect can be put forward. In the absence of stereoelectronic effects, alkyl substituents in AA and 9EA would stabilize the radical following deprotonation and thus enhance radical cation acidity. Such effects are evident in Russell's elegant study of steric effects in phenyl radical abstraction of hydrogen in toluene, ethylbenzene, and indane.[23] In Russell's case, since the phenethyl radical can readily become coplanar, hydrogen atom abstraction from ethylbenzene is faster than that for toluene by a factor of 3. However, this is not sufficient to account for the 28:1 preference in the anthracene radical cation series. Using compounds identical to ours, Tanko has studied hydrogen atom abstraction by bromine atom in a series of alkyl aromatics.[24] In his case, he observes relative rates of reaction for the series 9MA, AA, and 9EA of 1.0/11.3/0.06, differences which cannot be accounted for by the C−H bond dissociation energies for 9MA, 9EA, and AA of 82, 80, and 82 kcal/mol, respectively, calculated by the AM1 method. Tanko is forced to conclude that the difference in reactivity must be due to a stereoelectronic effect in the transition state. In our case, where the relative rates of 1.0/28/<0.001 are even more disparate, we are driven to similar but more forceful conclusions, with additional modifications.

One possible factor which may influence radical cation deprotonations is that the geometry of the radical cation may differ considerably from that of the neutral. In particular, the presence of large hyperfine coupling constants in 9-methylanthracene derivatives, presumably due to significant hyperconjugation, suggests that rehybridization in AA may place the CH_2 group more nearly perpendicular to the anthracene plane. Such hyperconjugation is not available to the ethylanthracenes. However, recent extensive *ab initio* calculations on toluene radical cation indicate that little such rehybridization does indeed take place.[25] An additional entropic factor may also be involved. That is, deprotonation of a methylaryl radical cation requires loss of one additional conformational degree of freedom over that for nucleophilic attack. It is important to note in this regard that, when the conformation is locked, as in AA or TMSMA, deprotonation becomes the dominant decay pathway.

(22) In separate experiments which are not described here, we have observed that 9,10-diethylanthracene undergoes oxidative substitution under identical reaction conditions at rates that are at least 100 times slower.

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Conclusions

The failure of strongly acidic alkylaryl radical cations to undergo facile deprotonation can now be understood on the basis of stereoelectronic factors rather than from any reluctance of these intermediates to act as strong acids. When conformations are carefully controlled, nucleophilic attack ceases to be the dominant pathway and deprotonation dominates. These observations have important consequences not only for the study of radical cations in general but also for their possible role in enzymatic oxidations, where the failure to observe side-chain oxidation pathways may reflect not the absence of radical cation intermediates but the unavailability of the requisite geometry for proton transfer.

Experimental Section

Materials. 9-Methylanthracene (9MA). 9-Methylanthracene was purchased from Aldrich Chemical Co. and recrystallized from hexane.

9-Ethylanthracene (9EA). 9-Ethylanthracene was synthesized in 79% yield by reaction of 9-bromoanthracene with ethylmagnesium chloride using $NiCl_2$(dppp)[21] catalyst in tetrahydrofuran. The product was recrystallized from methanol to yield pale yellow prisms, mp 62−63 °C (lit.[26] mp 63−64 °C).

Aceanthrene (AA). 3-Aceanthrone was synthesized according to the method of Scott.[19] The ketone was subjected to Wolff−Kischner reduction in refluxing ethylene glycol to yield aceanthrene in 56% yield. Recrystallization from methanol afforded yellow plates, mp 113−114 °C (lit.[20] mp 113−114 °C).

General Procedure for Iodine−Pyridine Oxidations. A 1.00 mmol portion of substituted anthracene and 4.00 g of iodine (15.8 mmol) were dissolved in 6 mL of pyridine and 10 mL of $CHCl_3$. After 24 h at room temperature, the mixture was diluted with 50 mL of $CHCl_3$, washed with saturated sodium thiosulfate, and concentrated. Ether (40 mL) was added; the precipitate was separated by centrifugation, washed with ether (2 × 40 mL), and dried in vacuo. The iodide was converted to the perchlorate by reaction with $LiClO_4$ in CH_3CN, precipitated by addition of water, and recrystallized from acetone or $CHCl_3$. Oxidation of some anthracenes often gave poor yields (<70%) presumably due to the production of dimeric species. In such cases, increased reaction times and elevated temperatures did not improve the yield of pyridinium iodides. Confirmation of this rationale was obtained from GC−MS analysis of the supernatant following precipitation. This procedure gave molecular ions of *m/e* 382 (base 191) for 9MA and *m/e* 404 (base 202) for aceanthracene, indicating the presence of dimeric species.[27]

Oxidation of 9-Methylanthracene. From 192 mg (1.00 mmol) of 9-methylanthracene, iodine (4.00 g, 15.8 mmol), pyridine (6 mL), and $CHCl_3$ (10 mL) was obtained 286 mg (0.72 mmol, 72%) of a mixture of pyridinium salts. The solid was redissolved in $CHCl_3$. A second precipitation with ether afforded 163 mg (41%) of a mixture consisting of *N*-(10-methyl-9-anthracenyl)pyridinium iodide (MAP) and *N*-(9-anthracenylmethyl)pyridinium iodide (AMP) in a 9:1 ratio. The relative amount of the two isomers was determined from the integrated NMR spectrum of the mixture by comparing the area of the H_4 and H_5 doublet of MAP at δ 7.22 with that of the CH_2 singlet at δ 6.97. After fractional recrystallization from $CHCl_3$, yellow plates of MAP were obtained, mp 249.5−250 °C. Spectral data: ^{1}H NMR (Me_2SO-d_6) δ 9.45 (2H, d, N=CH), 9.08 (1H, t, pyr), 8.63 (2H, d, arom), 8.56 (2H, t, arom), 7.78−7.66 (4H, m, arom), 7.22 (2H, d, arom), 3.26 (3H, s, CH_3); IR ($CHCl_3$) 3051, 3027, 2936, 1619, 1463, 1369, 1335, 1237(m), 746, 693(s) cm^{-1}; UV (CH_3OH) λ_{max} (log ϵ) 215 nm (4.67), 246 (4.75), 358 (3.93), 376 (4.04), 396 (3.95). Anal. Calcd for $C_{20}H_{16}NI$: C, 60.47; H, 4.06; N, 3.52; I, 31.94. Found: C, 59.82; H, 4.11; N, 3.45; I, 31.51.

The iodide was converted to its perchlorate and recrystallized from acetone to yield yellow plates. Single-crystal X-ray diffraction yielded the structure shown in ref 15. The NMR spectrum of the crude precipitate indicated, in addition to strong peaks for the pure material after recrystallization, a group of weak peaks identical with that of the independently prepared material.

Oxidation of Aceanthrene. From aceanthrene (204 mg, 1.00 mmol), iodine (4.00 g, 15.8 mmol), pyridine (6 mL), and $CHCl_3$ (10 mL) was obtained 279 mg (0.68 mmol, 68% total) of a mixture consisting of *N*-(4-aceanthryl)pyridinium iodide (4AAP-I) and *N*-(9-aceanthryl)pyridinium iodide (9AAP-I) in a 76:24 ratio. The relative amount of the two isomers was determined from the integrated NMR spectrum of the mixture by comparing the area of the doublet of doublets of 4AAP at δ 4.47 with that of the doublet of 9AAP at δ 3.95. After conversion of the mixture to the perchlorates and fractional recrystallization from acetone, reddish brown prisms of 4AAP perchlorate were obtained, mp 196−197 °C, and subjected to single-crystal X-ray diffractometry (see Figure 3).[28] Spectral data: ^{1}H NMR (Me_2SO-d_6) δ 8.97 (2H, d), 8.63 (1H, t of m), 8.58 (1H, d), 8.11 (2H, t), 8.07 (1H, m), 7.85 (1H, m), 7.75−7.68 (2H, m), 7.61−7.56 (3H, m), 7.52 (1H, d), 4.47 (1H, dd), 3.86 (1H, d); IR ($CHCl_3$) 3041, 2929, 1625, 1477, 1238, 1132(m), 745, 682(s) cm^{-1}; UV (CH_3OH) λ_{max} (log ϵ) 221 nm (3.93), 251 (4.14), 366 (3.34), 386 (3.50), 408 (3.57); MS *m/e* 258.2, 246.2, 230.2, 218.1, 202.1(100), 174.1, 150.1, 101.1, 79.1.

Oxidation of 9-Ethylanthracene. From 9-ethylanthracene (9EA; 103 mg, 0.500 mmol), iodine (2.00 g, 7.89 mmol), pyridine (3 mL), and $CHCl_3$ (5 mL) was obtained 88.0 mg (41.4%) of *N*-(9-ethyl-10-anthryl)pyridinium iodide (EAP), mp 223.5−224 °C, as yellow prisms after double precipitation. Spectral data: ^{1}H NMR (Me_2SO-d_6) δ 9.48 (2H, d), 9.09 (1H, t), 8.63 (2H, d), 8.57 (2H, t), 7.78−7.67 (4H, m), 7.23 (2H, d), 3.83 (2H, q), 1.44 (3H, t); IR ($CHCl_3$) 3062, 2971, 2929(m), 1618, 1463(s), 1456, 1372, 1238, 1160(m), 759, 660(s) cm^{-1}; UV (CH_3OH) λ_{max} (log ϵ) 216 nm (4.61), 252 (4.95), 359 (3.93), 377 (4.05), 397 (3.95). Anal. Calcd for $C_{21}H_{18}NI$: C, 61.33; H, 4.41; N, 3.41; I, 30.85. Found: C, 61.99; H, 4.45; N, 3.37; I, 30.24.

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