9-Alkylanthracene radical cations. An alternate route to apparent products of deprotonation

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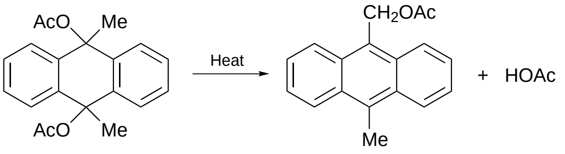
Side-chain oxidation products formed in the oxidation of 9-alkylanthracenes in MeOH–MeCN do not arise from radical cation deprotonation.

The removal of an electron from a hydrocarbon dramatically increases its acidity. For example, the pK_a of toluene drops from 41 to *ca.* −13 with the removal of a single electron. Consequently, there is a great deal of interest in the thermodynamic and kinetic acidity of radical cations.[1–4]

For an alkylaromatic radical cation, there are two competing pathways for reaction with a base (B:); side chain deprotonation (yielding a benzyl radical), and/or nucleophilic addition to the aromatic ring.[5–8] For alkylbenzenes, the side-chain deprotonation predominates. The effect of structure (of either the alkylbenzene or the base) on the rate of deprotonation has been extensively studied, and the deprotonation is believed to proceed *via* an early (reactant-like) transition state. Rate constants were successfully correlated to the Brønsted equation, with $\alpha \approx 0.25–0.30$.[4,9] The rate constant for deprotonation of $PhCH_3^{\bullet+}$ (H_2O as base) is approximately $1.0 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$.[6]

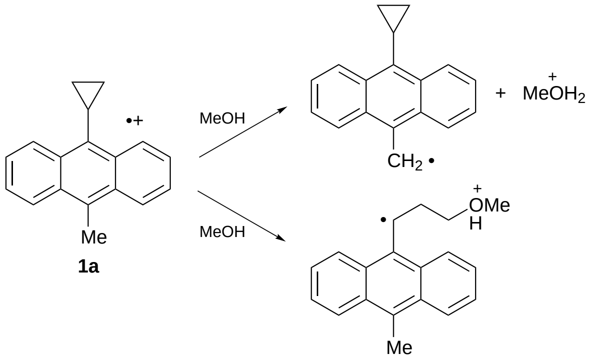
In the case of 9-alkylanthracenes, the situation is more complicated. Thermodynamically, these radical cations are quite acidic (9-methylanthracene is estimated to have a pK_a of *ca.* −6.4),[2] however the literature is somewhat contradictory in terms of the extent to which these radical cations undergo deprotonation. In 1970, Parker reported that radical cations generated from 9-alkyl- and 9,10-dialkyl-anthracenes lead mainly to products derived from nucleophilic addition of solvent (water, alcohol, acetic acid, *etc.*) to the aromatic ring.[10] Moreover, when HOAc was the solvent and at elevated temperatures, the initially formed addition products were observed to eliminate HOAc and rearrange to yield a 'side-chain oxidation' product [eqn. (1)].[10] Similarly, Camaioni and co-workers also found that a significant fraction of 'side-chain oxidation' products were derived from HOAc-addition products.[7,11] Others have generally ascribed the side-chain oxidation products as arising exclusively from deprotonation of a radical cation.[12,13]



(1)

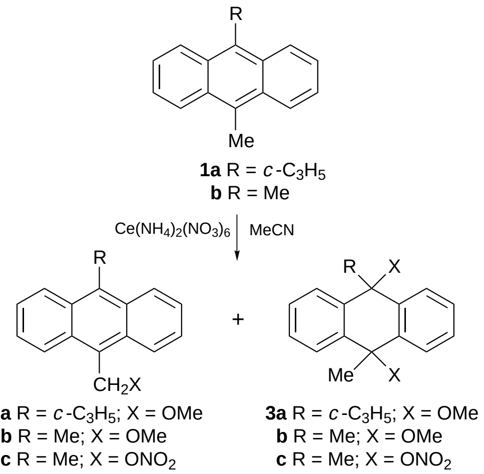
We became interested in this problem as the result of a continuing study of the chemistry of radical cations derived from cyclopropylarenes.[14] Initially, using the radical cation generated from 9-cyclopropyl-10-methylanthracene **1a**, we had hoped to use the deprotonation reaction in an intramolecular competition to clock the rate of methanol-induced cyclopropane ring opening (Scheme 1).

Treatment of **1a** with 1.9 equiv. of ceric ammonium nitrate in MeCN–MeOH at 45 °C led to side-chain oxidation product **2a** and ring-oxidation product **3a** (Scheme 2) in 37 and 57% yield, respectively. However, when the reaction was conducted at 0 °C, **3a** was formed in 91% yield, and no **2a** was detected (mass balances > 95%). This dramatic effect of temperature on the product ratio suggested that **2a** was *not* arising from the direct deprotonation of a radical cation.



Scheme 1

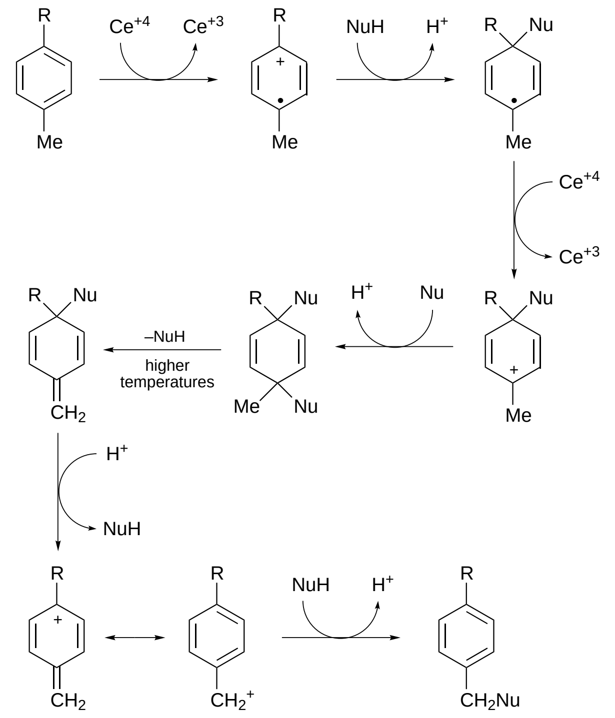
In order to test this hypothesis, 9,10-dimethylanthracene **1b** (Scheme 2) was treated with 1.9 equiv. of Ce^{IV} under a variety of conditions (Table 1), and essentially the same results were obtained: at 0 °C, only ring-oxidation product **3b** was found; at 45 °C approximately equal amounts of **2b** and **3b** were formed. In order to determine whether **2b** was formed from **3b**, the following control experiment was run: **1b** was allowed to react



Scheme 2

Table 1 Products arising from treatment of 9,10-dimethylanthracene with Ce^{IV} under various conditions

Reaction conditions	**2b** (%)	**3b** (%)
0 °C; 30 min	0.0	98.3
45 °C; 30 min	40.8	53.0
0 °C; 30 min	0.0	94.3
then		
45 °C; 30 min	43.0	49.0



Scheme 3 Note: To conserve space, only the central ring of the 9,10-disubstituted anthracene is shown

with Ce^{IV} at 0 °C for 30 min, and the reaction mixture was divided into two portions. The first portion was subject to work-up, and analyzed by ^{1}H NMR spectroscopy. The only product detected was **3b**. The second portion, which was warmed to 45 °C for 30 min and subsequently subject to the same work-up, was found to contain **2b** and **3b** in approximately the same ratio as when **1b** was reacted with Ce^{IV} at 45 °C.

The conversion **3b** → **2b** is apparently favored by higher reaction temperatures, and requires the presence of a Lewis acid. (**3b** is stable at 50 °C indefinitely. However, in the presence of a small amount of H$^+$, **3b** is quantitatively converted into **2b** within 15 min.)

In the absence of MeOH, oxidation of **1b** at 0 °C, followed by work-up, leads exclusively to side-chain oxidation product **2c**. However, the failure to isolate **3c** is likely because of its instability. Indeed, when the reaction was conducted in CD$_3$CN and analyzed by ^{1}H NMR *prior* to work-up, we found no resonances attributable to either **1b** or **2c**. We tentatively assign the observed resonances to **3c**. After work-up of the NMR sample, **2c** was the only observed product (85% yield). The presumed mechanism for these reactions is summarized in Scheme 3.

These results demonstrate that deprotonation (base = MeOH or NO$_3^-$) of 9-alkylanthracene radical cations is slow† relative to nucleophilic addition to the aromatic ring, and that little of the observed side-chain oxidation product can be attributed to deprotonation of the radical cation. The observed side-chain oxidation products actually arise from further reaction of the nucleophillic addition product. Conversion of this initially formed adduct to the side-chain oxidation product is facile in the presence of a Lewis acid and at higher reaction temperatures. Consequently, it is dangerous to draw mechanistic inferences pertaining to the deprotonation of 9-alkylanthracene radical cations based upon product analyses.‡

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Footnotes and References

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† The fact that deprotonation of radical cations is sluggish despite a potent thermodynamic driving force has been noted in the literature, see refs. 9 and 12.

‡ A reviewer has noted that our reaction conditions are non-aqueous, and that these observations may not apply to aqueous systems.

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