Radical ion probes. Part 10. Ceric(IV) ammonium nitrate oxidation of cyclopropylarenes†

Yonghui Wang and J. M. Tanko *

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212, USA

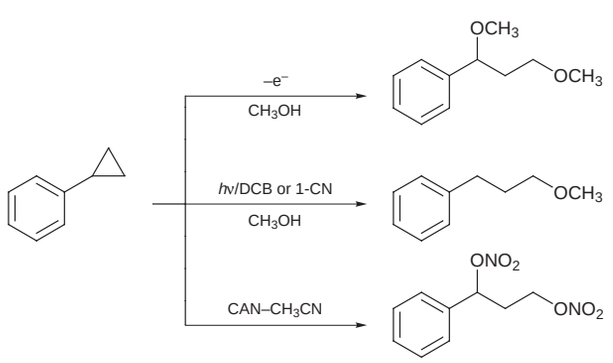
Received (in Gainesville, FL) 17th July 1998, Accepted 11th October 1998

The chemistry of radical cations generated *via* the oxidation of several cyclopropylarenes with ceric(IV) ammonium nitrate in CH_3CN–CH_3OH is reported. For cyclopropylbenzene, the major product is 1-phenylpropane-1,3-diyl dinitrate, arising from ring opening of the cyclopropylbenzene radical cation. Experiments with 1-cyclopropyl-4-methylbenzene reveal that ring opening of cyclopropylbenzenes occurs substantially faster than side chain deprotonation. Cyclopropane ring opened products are also formed in the oxidation of 1- and 2-cyclopropylnaphthalenes. For 9-cyclopropylanthracene however, ring opened products are not detected. Instead, all products arising from this reaction are attributable to reaction of nucleophiles with the aromatic ring. Overall, these results confirm and extend earlier observations pertaining to the chemistry of cyclopropylarene radical cations. General principles associated with the use of cyclopropyl groups as "probes" for radical cation intermediates, and general principles governing radical ion ring openings are discussed.

Introduction

The fate of a cyclopropyl group incorporated into a substrate participating in a chemical process often provides useful mechanistic information about the importance of radicals and/or radical ions as intermediates along the reaction pathway. Consequently, cyclopropane derivatives are frequently utilized as "probes" for radical cation intermediates in a number of important chemical and biochemical oxidations.[1–4] The implicit assumption in such studies is that if a radical cation is produced, it will undergo ring opening. However, earlier work dealing with ketyl radical *anions*[5–8] has shown that many of the analogous assumptions pertaining to the facility of ring opening of these species were incorrect. In this paper, the chemistry of radical cations generated from cyclopropylarenes is described.

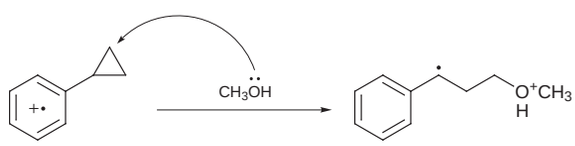
Anodic,[9] photochemical[10,11] and chemical oxidation[12,13] of cyclopropylbenzenes all led to cyclopropane ring-opened products (Scheme 1). Dinnocenzo *et al.*[14–17] have shown that



Scheme 1

ring opening of cyclopropylbenzene radical cation occurs *via* a nucleophile-induced (*i.e.*, S_N2) pathway (Scheme 2), which has been thoroughly characterized in terms of its stereochemistry, kinetics, regiochemistry and kinetic isotope effects.

The follow-up chemistry of radical cations generated from



Scheme 2

cyclopropylnaphthalenes was examined electrochemically.[18] Although anodic oxidation of 1- and 2-cyclopropylnaphthalenes in the presence of CH_3OH also led to cyclopropropane ring-opened products, the rate constant for methanol induced ring opening was estimated to be extremely small ($<20\ M^{-1}\ s^{-1}$) despite the fact that ring opening is exothermic by nearly 125 kJ mol^{-1}. These results were explained on the basis of a product-like transition state for ring opening wherein the positive charge is localized on the cyclopropyl group, and thus unable to benefit from potential stabilization offered by the aromatic ring.

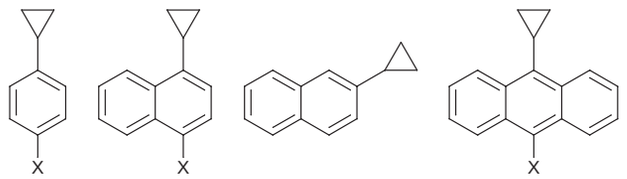
Reactions of radical cations generated from 9-cyclopropylanthracenes in CH_3CN–CH_3OH have also been investigated electrochemically.[19] The major products arising from oxidation of these anthryl substrates are attributable to CH_3OH attack at the aromatic ring rather than CH_3OH-induced cyclopropane ring opening.

Because of the nature of the electrochemical experiment, radical cations are generated heterogeneously and in high concentration near the electrode surface and as a result, dimerization or coupling processes often predominate. The products isolated from electrolyses of cyclopropylnaphthalenes were mainly cyclopropane ring-opened monomeric and dimeric products, and the radical cations of cyclopropylnaphthalenes were found to decay *via* a process *second-order* in radical cation. Thus it is important to augment the results of these electrochemical experiments by utilizing other methods of radical cation generation.

Cerium(IV) is a well-characterized one-electron oxidant. Ceric ammonium nitrate (CAN) oxidation of alkyl aromatic compounds has been extensively studied. For example, side-chain oxidations of alkylbenzenes[20–24] have been studied in term of mechanism, kinetics, stereoelectronic and substituent effects, *etc*.

† For Part 9, see ref. 19.

In this paper, results pertaining to the *homogeneous* CAN oxidation of several cyclopropylarenes in CH_3CN–CH_3OH are reported. The cyclopropane-containing substrates chosen for study include 1-cyclopropylbenzene (**1**), 1-cyclopropyl-4-methylbenzene (**2**), 1-cyclopropylnaphthalene (**3**), 1-bromo-4-cyclopropylnaphthalene (**4**), 2-cyclopropylnaphthalene (**5**), 9-cyclopropylanthracene (**6**) and 9-bromo-10-cyclopropylanthracene (**7**).

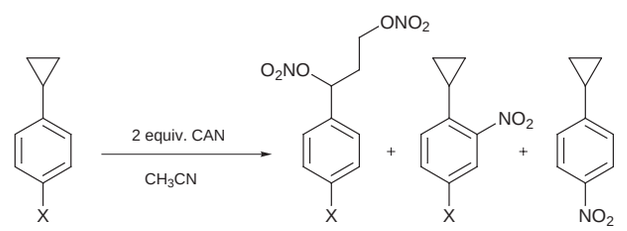


1 (X = H)
2 (X = CH_3)
3 (X = H)
4 (X = Br)
5
6 (X = H)
7 (X = Br)

Results and discussion

CAN oxidation of 1-cyclopropylbenzene (1) and 1-cyclopropyl-4-methylbenzene (2)

CAN oxidation of **1** in CH_3CN mainly produces cyclopropane ring-opened 1-phenylpropane-1,3-diyl dinitrate (**8**, 60.7%); aromatic nitration products, 1-cyclopropyl-2-nitrobenzene (**9**, 20%) and 1-cyclopropyl-4-nitrobenzene (**10**, 7.5%) are also obtained as by-products. (Similar results were reported by Young[12] and Ouellette).[13] Under the same conditions, CAN oxidation of **2** yields as the major product 1-(4-methylphenyl)-propane-1,3-diyl dinitrate (**11**, 67.4%) and a small amount of 1-cyclopropyl-4-methyl-2-nitrobenzene (**12**, 12.8%, Scheme 3).



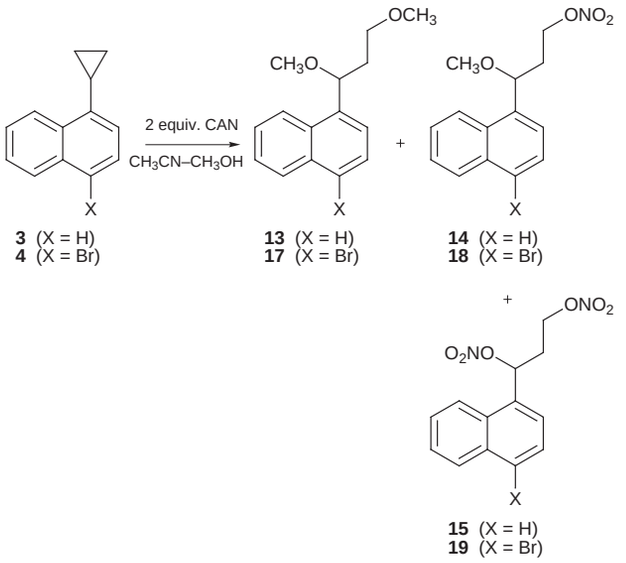
1 (X = H)
2 (X = CH_3)
8 (X = H)
11 (X = CH_3)
9 (X = H)
12 (X = CH_3)
10

Scheme 3

No products attributable to side-chain deprotonation were detected. For comparison, the CAN oxidation of toluene was performed under identical conditions. The oxidation was extremely sluggish (87% of the starting material was recovered after the same period of reaction time) and less than 1% of side-chain deprotonation product (benzyl nitrate) was detected by ^{1}H NMR. These results clearly show that cyclopropane ring opening of $\mathbf{2}^{\bullet+}$ is much faster then deprotonation of this radical cation.

CAN oxidation of 1-cyclopropylnaphthalene (3), 1-bromo-4-cyclopropylnaphthalene (4) and 2-cyclopropylnaphthalene (5)

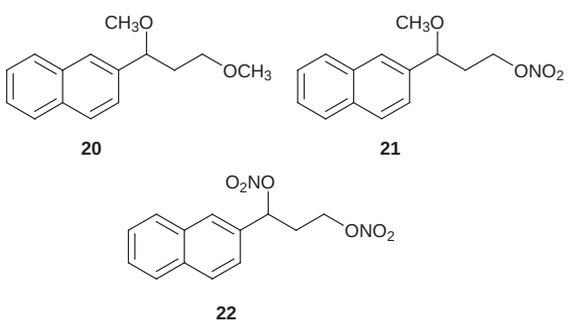
CAN oxidation of **3** in CH_3CN–CH_3OH mainly yielded cyclopropane ring-opened 1,3-disubstituted products: 1-(1,3-dimethoxypropyl)naphthalene (**13**), 3-methoxy-3-(1-naphthyl)-propyl nitrate (**14**), and 1-naphthylpropane-1,3-diyl dinitrate (**15**) (Scheme 4). In the absence of methanol, CAN oxidation of **3** in CH_3CN gave 47% of **15** as the major product (with 18% of **3** recovered). It was noted that 3-hydroxy-3-(1-naphthyl)propyl nitrate (**16**) was formed from **15** during chromatographic separation. Like **3**, CAN oxidation of **4** in CH_3CN–CH_3OH yielded mainly cyclopropane ring-opened products, **17**, **18** and **19** (Scheme 4).



3 (X = H)
4 (X = Br)
13 (X = H)
17 (X = Br)
14 (X = H)
18 (X = Br)
15 (X = H)
19 (X = Br)

Scheme 4

CAN oxidation of **5** in CH_3CN–CH_3OH yielded similar cyclopropane ring opened products, **20**, **21** and **22**. 3-Hydroxy-3-(2-naphthyl)propyl nitrate (**23**) was also formed during chromatographic separation. The product yields are summarized in Table 1.



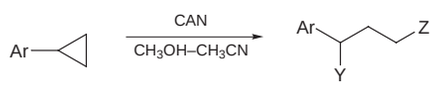
20
21
22

CAN oxidation of 9-cyclopropylanthracene (6) and 9-bromo-10-cyclopropylanthracene (7)

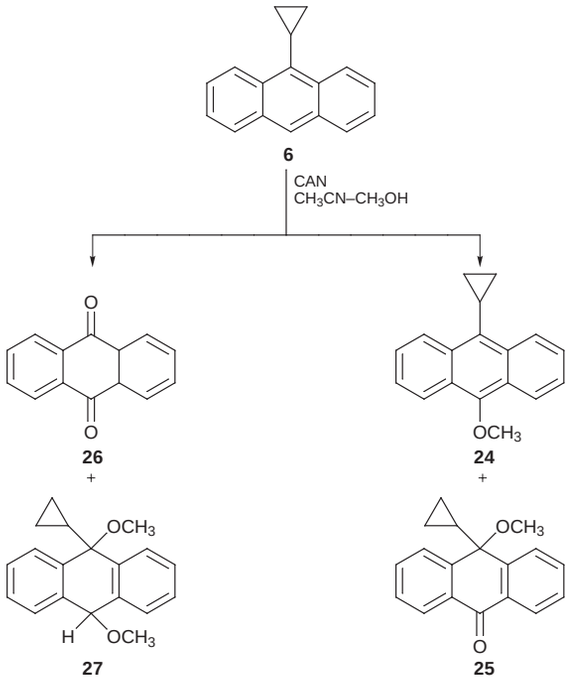
CAN oxidation of **6** in 9:1 (v/v) CH_3CN–CH_3OH at room temperature produces mainly 9-cyclopropyl-10-methoxyanthracene (**24**) and 9-cyclopropyl-9-methoxyanthrone (**25**). Some anthraquinone (**26**) and 9,10-dimethoxy derivative (**27**) were also formed (Scheme 5). For **7** under similar conditions, **25** is produced as the major product. The results are summarized in Table 2. The nature of the products and yields are similar to those observed in the electrochemical oxidation of these substrates.[19]

Because CAN is a *one-electron* oxidant, the mole ratio CAN : substrate reflects the number of electrons transferred. The effect of the CAN : **6** mole ratio on the product distribution is shown in Table 3. These results suggest that the initially

Table 1 Products and yields (%, isolated) associated with the CAN oxidation of **3**, **4** and **5**



Substrate	Unreacted substrate	Y = OCH_3 Z = OCH_3	Y = OCH_3 Z = ONO_2	Y = ONO_2 Z = ONO_2
3	22.0	20.4	35.0	9.1
4	25.2	14.0	33.3	15.6
5	11.6	18.6	22.4	33.5



Scheme 5

Table 2 Product yields (%)[a] of CAN oxidation of **6** and **7** in CH_3CN–CH_3OH

Substrate	Mole ratio[b]	**24**	**25**	**26**	**27**
6	2[c]	29	17	9	9
	4	22	48	21[d]	2[d]
7	2	—	60	9[d]	—
	2	—	76[e]	8[d]	—

[a] Isolated yields unless otherwise indicated. [b] Mole ratio of CAN to substrate. [c] 10% of **6** recovered after reaction. [d] GC yield. [e] HPLC yield.

Table 3 Product distribution in the CAN oxidation of **6** at various CAN:**6** mole ratios

Substrate (mmol)	Mole ratio (CAN:**6**)	Yields (%)[a] **6**	**24**	**25**
0.025	1	61	8	2
0.025	2	29	38	10
0.025	3	0	31	22
0.025	4	0	21	43

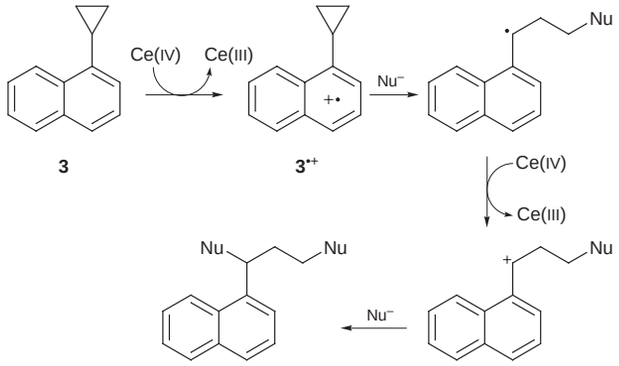
[a] HPLC yields, only **6**, **24**, **25** were analyzed.

formed two electron product **24** is further oxidized under the reaction conditions to four-electron oxidation product **25**. For the oxidation of **7**, two moles of electrons are needed to form product **25**.

Proposed CAN oxidation mechanism

The mechanism for the oxidation of cyclopropylnaphthalenes is assumed to be similar to that of cyclopropylbenzenes. The radical cation $\mathbf{3}^{\bullet+}$ undergoes nucleophile-induced (Nu = CH_3OH, ONO_3^-) cyclopropane ring opening to form a benzylic-type radical,[10,16] which is further oxidized to the corresponding cation. This cation is then captured by a second molecule of nucleophile to give 1,3-disubstituted product (Scheme 6).

Under electrochemical conditions, $\mathbf{3}^{\bullet+}$ decays by a rate law which is second-order in radical cation, and alternative mechanisms have been proposed for anodic oxidation of cyclopropylnaphthalenes:[18] a) Dimerization pathway—radical



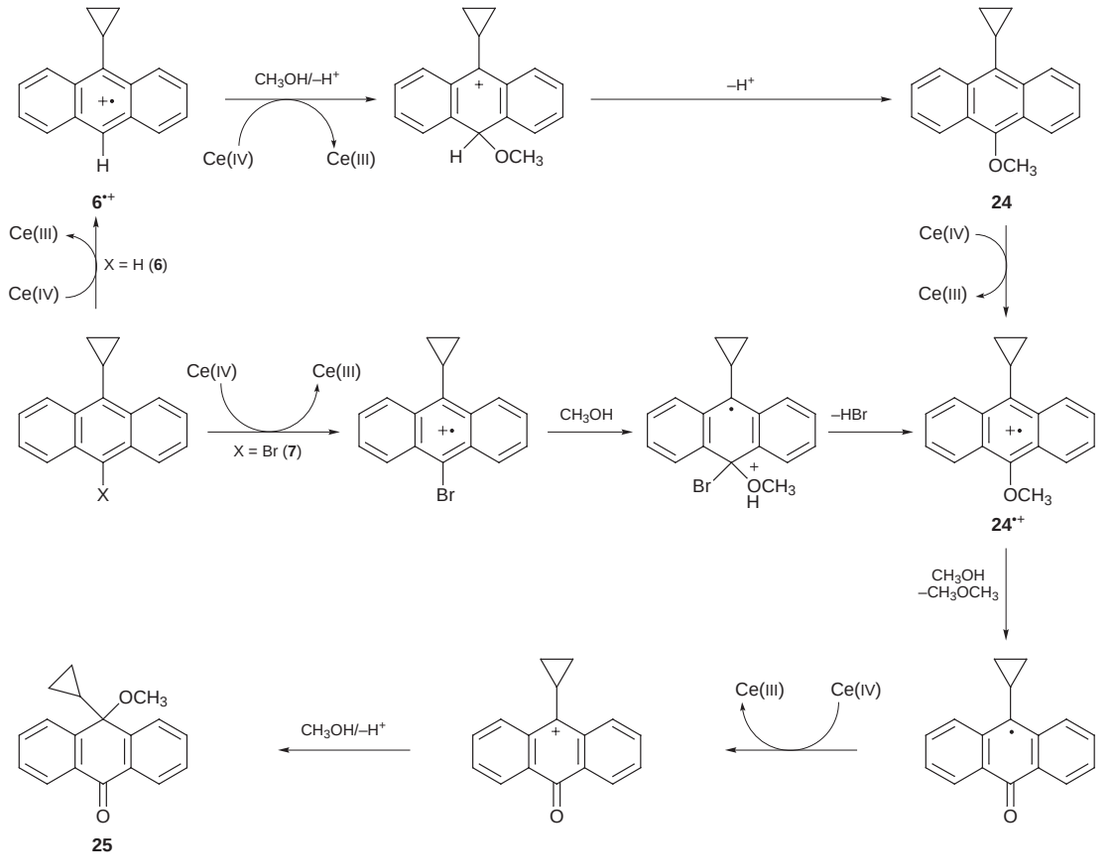
Scheme 6

cation $\mathbf{3}^{\bullet+}$ dimerizes to form dimer dication, which experiences nucleophile attack to form benzylic-type cation and release neutral **3**. The cation is captured by nuclophile to give 1,3-disubstituted product. b) Disproportionation pathway—two radical cations of **3** disproportionate to a neutral **3** and dication $\mathbf{3}^{2+}$, which is attacked by methanol to lead to the same product. Regardless of which of these mechanisms is correct, the results clearly show that the rate of this second-order process is significantly greater than the rate of nucleophile-induced cyclopropane ring opening.

The proposed oxidation mechanism for **6** and **7** is summarized in Scheme 7. Radical cation $\mathbf{6}^{\bullet+}$ can be either attacked by CH_3OH (followed by oxidation) or undergo disproportionation to a dication (followed by CH_3OH attack to form a methoxy substituted cation). Our electrochemical experiments[19] and results from Fujita and Fukuzumi's Fe(III) oxidation of 9-benzylanthracene revealed that the 9-substituted anthracene radical cation undergoes disproportionation[25] to give the corresponding dication, which is captured by methanol to form the methoxy substituted cation followed by rapid proton loss to produce **24**. From **6** to **24**, two electrons must be transferred. Radical cation $\mathbf{24}^{\bullet+}$ demethylates[26] to a ketyl radical which undergoes further oxidation to the corresponding cation, followed by methanol attack to form **25**. From **24** to **25**, two more electrons must be transferred (Scheme 7). For **7**, it is a radical cation or dimer radical cation (complex)[19] that is attacked by methanol based on our electrochemical results. The mechanism is supported by the fact that HBr was noted in the reaction and no **24** was detected. From **7** to **25**, a two electron transfer is needed (Scheme 7). The final product **25** is similar to those obtained from oxidation[27] of 9-phenylanthracene and 9-bromo-10-phenylanthracene.

Effect of aryl groups on reactivity of cyclopropylarene radical cations

Unlike cyclopropylbenzenes and cyclopropylnaphthalenes, radical cations generated from **6** and **7** do not experience methanol-induced cyclopropane ring opening. The reasons for the lack of reactivity of the cyclopropyl group were discussed earlier;[18] a product-like transition state for ring opening of cyclopropylarene radical cations was proposed, in which spin density is delocalized over C-1 (the benzylic carbon) and the aromatic ring, but charge is highly localized at C-2 and oxygen. As such, in the transition state, the aryl group can stabilize the radical portion of the developing distonic radical ion (presumably to a lesser degree than for the fully developed radical), but will have little effect on the positive charge. Consequently, the effect of the aromatic ring on the rate is primarily due to changes in the free energy of the reactant, with only a modest effect on the free energy of the transition state for ring opening. The effects of aryl rings on the stabilities of reactants, transition states and products for methanol-induced cyclo-



Scheme 7

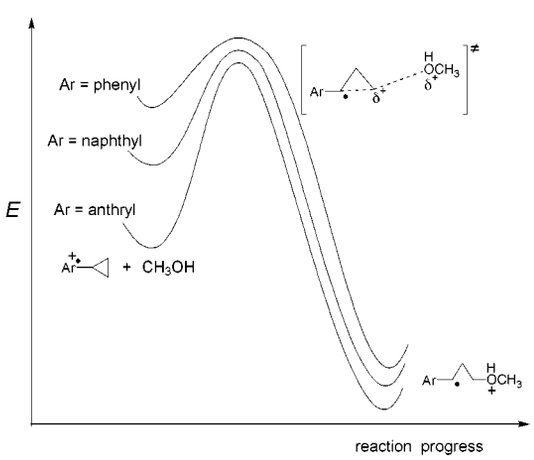


Fig. 1 The proposed effects of aryl rings on the stabilities of reactants, transition states and products for methanol-induced ring opening of cyclopropylarenes.

propane ring opening are shown in Fig. 1. Because of a higher intrinsic barrier to nucleophile-induced cyclopropane ring opening of these anthryl radical cations, nucleophilic addition occurs predominantly.

Suitability of cyclopropylarenes as SET probes

Cyclopropane-containing substrates are frequently employed as probes for single electron transfer. The implicit assumption in such a study is that if a paramagnetic intermediate (neutral free radical or radical ion) is produced, it will undergo ring opening. Earlier work dealing with neutral free radicals and ketyl radical anions has shown that the rate constant for ring opening is quite large when the ring-opening is thermodynamically favored.[28,29]

In the case of cyclopropylarene radical cations, despite the fact that ring opening enjoys an enormous thermodynamic driving force, the process occurs at a dramatically lower rate (for the naphthyl system) or not at all (for the anthryl system). Clearly, the intrinsic barrier to ring opening is greater for ring opening of these radical cations. The unique activation/driving force relationship for radical cation ring opening is likely attributable to the fact that the process is bimolecular (nucleophile-assisted). The rate of ring opening is governed by the amount of positive charge transmitted to the cyclopropane ring *via* resonance, and the fact that this charge becomes localized in the transition state (Fig. 1). For neutral radicals or ketyl anions, it is spin rather than charge which is transmitted to the cyclopropyl group upon ring opening. Because ring opening is unimolecular, spin (and charge for the radical anions) is not localized in the transition state and the intrinsic barrier to ring opening is considerably lower. For cyclopropylarene radical cations, and presumably other systems which would undergo nucleophile-assisted ring opening, the fact that the ring opening reaction may enjoy a potent thermodynamic driving force is no guarantee that the ring opening will occur at an appreciable rate. Indeed, it is likely that many of the substrates discussed herein would fail to detect a *bona fide* SET process. Thus, these results reveal a new (and unexpected) complication in the design and utilization of SET probes.

Conclusions

1. CAN oxidation of cyclopropylbenzene (**1**) leads to cyclopropane ring-opened products, consistent with earlier reports. The products obtained from the oxidation of 1-cyclopropyl-4-methylbenzene (**2**) demonstrate that for $\mathbf{2}^{\bullet+}$, cyclopropane ring opening occurs at a much greater rate than side-chain deprotonation, despite the high acidity of the benzylic hydrogens ($pK_a \approx -20$).[30]

2. CAN oxidation of α- and β-cyclopropylnaphthalene also yields radical cations which undergo cyclopropane ring opening. However, these reactions proceed at substantially lower rates.

3. CAN oxidation of 9-cyclopropylanthracene yields a radical cation which does *not* undergo cyclopropane ring opening.

4. These observations using CAN as a chemical oxidant unify the results obtained from earlier electrochemical and photochemical studies, and support the proposal that the transition state for ring opening of cyclopropylarene radical cations is *product-like* (in terms of the distribution of charge and spin).

Experimental

General

Nuclear magnetic resonance spectra (^{1}H, ^{13}C) were obtained on a 400 MHz Varian FT NMR spectrometer. All chemical shifts are reported in δ units relative to TMS for qualitative analysis and $(CH_3)_3SiOSi(CH_3)_3$ ($\delta = 0.07$ *vs.* TMS) for quantitative analysis in $CDCl_3$. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. IR bands were reported in units of cm^{-1}. Mass spectra data were obtained from a Fisons VG Quattro triple quadrupole mass spectrometer. Gas chromatographic analyses were performed on a Hewlett Packard HP 5890A instrument equipped with FID detector, and an HP 3393A reporting integrator. Analyses were accomplished on an Alltech Econo-CAP SE-54 capillary column (30 × 0.25 mm). High-pressure liquid chromatography was performed in a Backman system Gold (model 128 solvent pump system and model 166 UV–VIS detector). Samples were separated using Backman C-19 reverse phase columns (analytical: 4.6 mm × 250 mm) with acetonitrile–water solvent mixtures. Flash chromatography (Merck, grade 9385 silica gel, 230–400 mesh, 60 Å) and thin layer chromatography (anal.: Whatman, silica gel plates, 250 μm layer, UV_{254}; prep.: Analtech, Silica Gel G & GF Preparative UNIPLATES, 20 × 20 cm, 500 microns) were performed using the solvent systems specified in the specific experiments.

Materials

$(NH_4)_2Ce(NO_3)_6$ (Aldrich) was dried under vacuum before use. CH_3CN (Mallinckrodt, HPLC grade, 99+%) was stirred over calcium hydride (Aldrich) until the cessation of gas evolution, refluxed over calcium hydride for at least one hour, then distilled slowly, discarding the first 5 and last 10% of distillate. CH_3OH (Baker Analyzed HPLC) was dried by stirring over calcium hydride, followed by distillation before use. 1-Cyclopropyl-4-methylbenzene was synthesized from 1-methyl-4-vinylbenzene (Aldrich) based on Simmons–Smith reaction.[31] 1-Cyclopropylnaphthalene,[32] 2-cyclopropylnaphthalene[32] and 9-cyclopropylanthracene[33] were prepared according to literature procedures. 1-Bromo-4-cyclopropylnaphthalene and 9-bromo-10-cyclopropylanthracene were prepared by dark bromination[34] of 1-cyclopropylnaphthalene and 9-cyclopropylanthracene, respectively.

CAN oxidation of cyclopropylbenzenes

Into 3 vials equipped with a magnetic stir bar were introduced 100 μL 1-cyclopropyl-4-methylbenzene (**2**) (80 mg, 0.6 mmol), cyclopropylbenzene (**1**) (94 mg, 0.8 mmol) and toluene (86 mg, 0.94 mmol), respectively. 5 mL CH_3CN was then added to each vial. To each solution, two equiv. of CAN were introduced (660 mg, 877 mg and 1030 mg, respectively). The three vials were heated to 75–80 °C for 5 minutes with stirring. For the cyclopropane derivatives, the white solid (Ce(III) salt) gradually formed during reaction, but for toluene, no obvious reaction occurred (the orange color of the solution persisted and no precipitate formed).

The reaction mixtures were extracted with ether and washed 4 times with water. The organic layer was dried over $MgSO_4$ and evaporated. 1 mL $CDCl_3$ and a measured amount of internal standard, $(CH_3)_3OSiO(CH_3)_3$, was added. Product yields were determined by ^{1}H NMR analysis.

The product mixture was then separated *via* preparative thin layer chromatography (PTLC). For cyclopropylbenzene, PTLC using hexane–ethyl acetate (10 : 1) as solvent gave pure 1-phenylpropane-1,3-diyl dinitrate (**8**) and a mixture of 1-cyclopropyl-2-nitrobenzene (**9**) and 1-cyclopropyl-4-nitrobenzene (**10**), which was subsequently separated with PTLC using hexane–$CHCl_3$ (2 : 1) as solvent. The spectral features of these compounds were consistent with earlier reports.[12,13]

For 1-cyclopropyl-4-methylbenzene, PTLC using hexane–ethyl acetate (10 : 1) as solvent gave 1-(4-methylphenyl)propane-1,3-diyl dinitrate and 1-cyclopropyl-2-nitro-4-methylbenzene. It was noted that 1,3 dinitrates can be converted to 1-(4-methylphenyl)-1-hydroxypropyl nitrate if left on the PTLC plate for a period of time.

The products were characterized as the following:

a) 1-(4-Methylphenyl)propane-1,3-diyl dinitrate (11).[35] (67.4%) ^{1}H NMR δ 2.21 (1H, m), 2.37 (3H, s), 2.41 (1H, m), 4.41 (1H, m), 4.56 (1H, m), 5.88 (1H, t), 7.23 (4H, dd); ^{13}C NMR δ 21.2 (CH_3), 31.8 (CH_2), 68.5 (CH_2), 81.4 (CH), 126.4 (CH, aromatic), 129.8 (CH, aromatic), 133.3 (C, aromatic), 139.6 (C, aromatic); IR ($CHCl_3$) *v* 1641 (s), 1281 (s), 1216, 908, 849; MS(EI) *m/e* 256 (M^+, 2.6), 194 ($M^+ - ONO_2$, 1.3), 164 (7.8), 119 (100); HRMS(EI) $C_{10}H_{12}O_6N_2$, calc. 256.0695, exp. 256.0705, error 3.7 ppm.

b) 1-Cyclopropyl-2-methyl-4-nitrobenzene (12).[35] (12.8%) ^{1}H NMR δ 0.65 (2H, m), 1.00 (2H, m), 2.34 (1H, m), 2.36 (3H, s), 7.04 (1H, d), 7.27 (1H, d), 7.61 (1H, s); ^{13}C NMR δ 7.7 (CH_2), 12.2 (CH), 20.6 (CH_3), 124.3 (CH, aromatic), 127.9 (CH, aromatic), 133.3 (CH, aromatic), 134.9 (C, aromatic), 136.6 (C, aromatic); IR *v* 1530 (s), 1350 (s); MS(CI) *m/e* 178 (MH^+, 37); MS(EI) 177 (M^+, 2.6), 149 (37), 128 (47), 115 (93); HRMS(CI) $C_{10}H_{12}O_2N_1$, calc. 178.0868, exp. 178.0874, error 3.1 ppm.

CAN oxidation of cyclopropylnaphthalenes

1-Cyclopropylnaphthalene (3). Into a 50 mL round-bottomed flask was added 33.6 mg (0.2 mmol) of 1-cyclopropylnaphthalene and 10 mL CH_3CN–CH_3OH (9 : 1, v/v) under N_2. 219.2 mg (0.4 mmol) of CAN was introduced into the flask. The reaction mixture was refluxed at 55 °C for 10 hours and then poured into diethyl ether and water for work-up. The ether extract was dried over $MgSO_4$ and evaporated. PTLC using 7 : 1 (v/v) hexane–EtOAc as solvent gave 7.4 mg (22%) of starting material 1-cyclopropylnaphthalene, 18.3 mg (35%) 3-methoxy-3-naphthylpropyl nitrate and a mixture of 1-naphthylpropane-1,3-diyl dinitrate, 3-hydroxy-3-naphthylpropyl nitrate and 1-naphthyl-1,3-dimethoxypropane.[18] A second PTLC of the latter mixture with $CHCl_3$ as solvent yielded 9.4 mg (20.4%) of 1-naphthyl-1,3-dimethoxypropane, 2.75 mg (4.7%) 1-naphthylpropane-1,3-diyl dinitrate and 2.15 mg (4.4%) of 3-hydroxy-3-naphthylpropyl nitrate. It was noted that 3-hydroxy-3-naphthylpropyl nitrate was produced in PTLC from 1-naphthylpropane-1,3-diyl dinitrate.

*a) 3-Methoxy-3-(1-naphthyl)propyl nitrate (**14**).* ^{1}H NMR δ 2.27 (2H, m), 3.31 (3H, s), 4.55 (1H, m), 4.74 (1H, m), 5.04 (1H, t), 7.53 (3H, m), 7.82 (1H, d), 7.91 (1H, d), 8.13 (1H, d); ^{13}C NMR δ 34.7 (CH_2), 57.0 (CH_3O), 70.4 (CH_2), 77.7 (CH), 122.8 (CH, aromatic), 123.9 (CH, aromatic), 125.4 (CH, aromatic), 125.7 (CH, aromatic), 126.3 (CH, aromatic), 128.4 (CH, aromatic), 129.1 (CH, aromatic), 130.8 (C, aromatic), 134.0 (C, aromatic), 136.1 (C, aromatic); IR *v* 1633 (s, O–N asymmetric stretching), 1281 (s, O–N symmetric stretching), 1113, 862 (p bond N–O linkage); MS(EI) *m/e* 262 (M + 1, 1.3), 261 (M^+, 11), 171 ($M - CH_2CH_2ONO_2$, 100), 153 (54), 127

(29); HRMS(EI) $C_{14}H_{15}O_4N$, exp. 261.0994, calc. 261.1001, error −2.5 ppm.

*b) 1-Naphthylpropane-1,3-diyl dinitrate (**15**).* ^{1}H NMR δ 2.48 (2H, m), 4.48 (1H, m), 4.66 (1H, m), 6.71 (1H, t), 7.56 (3H, m), 7.9 (2H, m), 8.06 (1H, d); ^{13}C NMR δ 31.9 (CH_2), 68.6 (CH_2), 78.4 (CH), 121.9 (CH, aromatic), 123.5 (CH, aromatic), 125.4 (CH, aromatic), 126.3 (CH, aromatic), 127.2 (CH, aromatic), 129.3 (CH, aromatic), 129.8 (C, aromatic), 129.9 (CH, aromatic), 132.6 (C, aromatic), 133.7 (C, aromatic); IR ($CHCl_3$) *v* 3021, 1647 (s), 1281, 1215 (s); MS(EI) *m/e* 292 (15.7), 127 (100); HRMS(EI) $C_{13}H_{12}O_6N_2$, calc. 292.0695, exp. 292.0688, error −2.5 ppm.

*c) 3-Hydroxy-3-(1-naphthyl)propyl nitrate (**16**).* ^{1}H NMR δ 2.07 (1H, d, OH), 2.31 (2H, m), 4.62 (1H, m), 4.81 (1H, m), 5.66 (1H, m), 7.53 (3H, m), 7.68 (1H, d), 7.82 (1H, d), 7.91 (1H, d), 8.06 (1H, d); ^{13}C NMR δ 35.1 (CH_2), 67.6 (CH), 70.5 (CH_2), 122.6 (CH, aromatic), 122.7 (CH, aromatic), 125.4 (CH, aromatic), 125.8 (CH, aromatic), 126.5 (CH, aromatic), 128.6 (CH, aromatic), 129.1 (CH, aromatic), 129.9 (C, aromatic), 133.8 (C, aromatic), 139.0 (C, aromatic); IR ($CHCl_3$) *v* 3601 (-OH), 3018, 1633, 1281, 1216 (s); MS(EI) *m/e* 248 (M + 1, 2.6), 247 (M, 26), 230 (M − OH, 6.5), 157 (M − $CH_2CH_2ONO_2$, 88), 129 (100); HRMS(EI) $C_{13}H_{13}O_4N$, calc. 247.0845, exp. 247.083969, error −2.0 ppm.

1-Bromo-4-cyclopropylnaphthalene (4). Into a 50 mL round-bottomed flask was added 49.2 mg (0.2 mmol) of 1-bromo-4-cyclopropylnaphthalene and 10 mL CH_3CN–CH_3OH (9:1, v/v) under N_2. 219.2 mg (0.4 mmol) of CAN was introduced into the flask and the reaction mixture was refluxed at 55 °C for 9 hours. The reaction mixture was extracted with ether and washed with water. The ether layer was dried over $MgSO_4$ and evaporated. PTLC using 7:1 (v/v) hexane–EtOAc as solvent gave 12.4 mg (25.2%) of starting material 1-bromo-4-cyclopropylnaphthalene, 22.6 mg (33.3%) 3-methoxy-3-(4-bromo-1-naphthyl)propyl nitrate and a mixture of 1-(4-bromo-1-naphthyl)propane-1,3-diyl dinitrate and 1-(4-bromo-1-naphthyl)-1,3-dimethoxypropane.[18] A second PTLC of the latter mixture with $CHCl_3$ as solvent yielded 8.64 mg (14%) of 1-(4-bromo-1-naphthyl)-1,3-dimethoxypropane and 11.66 mg (15.6%) 1-(4-bromo-1-naphthyl)propane-1,3-diyl dinitrate.

*a) 3-Methoxy-3-(4-bromo-1-naphthyl)propyl nitrate (**18**).* ^{1}H NMR δ 2.24 (2H, m), 3.30 (3H, s), 4.56 (1H, m), 4.74 (1H, m), 5.01 (1H, t), 7.41 (1H, d), 7.60 (2H, m), 7.81 (1H, d), 8.11 (1H, d), 8.34 (1H, d); ^{13}C NMR δ 34.8 (CH_2), 57.1 (CH_3O), 70.2 (CH_2), 77.3 (CH), 123.05 (CH, aromatic), 123.1 (C, aromatic), 124.3 (CH, aromatic), 127.16 (CH, aromatic), 127.18 (CH, aromatic), 128.3 (CH, aromatic), 129.7 (CH, aromatic), 131.97 (C, aromatic), 132.2 (C, aromatic), 136.4 (C, aromatic); IR ($CHCl_3$) *v* 3018, 1632 (s, O–N asymmetric stretching), 1280 (s, O–N symmetric stretching), 1116 (s), 1112, 866 (p bond N–O linkage); MS(EI) *m/e* 341 (M + 2, 9.0), 339 (M^+, 8.6), 251 (M + 2-$CH_2CH_2ONO_2$, 100), 249 (M − 90, 97), 156 (45), 152 (69); HRMS(EI) $C_{14}H_{14}O_4NBr$, exp. 339.0114, calc. 339.0106, error 2.2 ppm.

*b) 1-(4-Bromonaphthyl)propane-1,3-diyl dinitrate (**19**).* ^{1}H NMR δ 2.45 (2H, m), 4.49 (1H, m), 4.67 (1H, m), 6.67 (1H, t), 7.44 (1H, d), 7.67 (2H, m), 7.82 (1H, d), 8.06 (1H, m), 8.37 (1H, m); ^{13}C NMR δ 31.9 (CH_2), 68.4 (CH_2), 77.8 (CH), 122.2 (CH, aromatic), 123.7 (CH, aromatic), 124.8 (C, aromatic), 127.8 (CH, aromatic), 128.1 (CH, aromatic), 128.6 (CH, aromatic), 129.6 (CH, aromatic), 130.9 (C, aromatic), 132.2 (C, aromatic), 132.9 (C, aromatic); IR ($CHCl_3$) *v* 3018, 1645 (s), 1279, 1215 (s), 850; MS(EI) *m/e* 372 (M + 2, 3.6), 370 (M^+, 3.3), 280 (M − 90, 7.8), 278 (M + 2 − 90, 7.5), 233 (32), 152 (100); HRMS(EI) $C_{13}H_{11}O_6N_2Br$, calc. 369.9800, exp. 369.9807, error 1.8 ppm.

2-Cyclopropylnaphthalene (5). Into a 50 mL round-bottomed flask was added 33.6 mg (0.2 mmol) of 2-cyclopropylnaphthalene and 10 mL CH_3CN–CH_3OH (9:1, v/v) under N_2. 219.2 mg (0.4 mmol) of CAN was introduced and the reaction mixture was refluxed at 55 °C for 11 hours. The reaction mixture was extracted with ether, washed with water, and the ether layer dried over $MgSO_4$ and evaporated. PTLC using 3:1 (v/v) hexane–EtOAc as solvent gave 3.9 mg (11.6%) recovered starting material 2-cyclopropylnaphthalene, 11.7 mg (22.4%) of 3-methoxy-3-(2-naphthyl)propyl nitrate, 8.56 mg (18.6%) of 1-(2-naphthyl)-1,3-dimethoxypropane[18] and a mixture of 1-(2-naphthyl)propane-1,3-diyl dinitrate and 3-hydroxy-3-(2-naphthyl)propyl nitrate. A second PTLC of the latter mixture with $CHCl_3$ as solvent yielded 9.58 mg (16.4%) of 1-(2-naphthyl)propane-1,3-diyl dinitrate and 8.45 mg (17.1%) of 3-hydroxy-3-(2-naphthyl)propyl nitrate. It was noted that 3-hydroxy-3-(2-naphthyl)propyl nitrate was produced in PTLC from 1-(2-naphthyl)propane-1,3-diyl dinitrate.

*a) 3-Methoxy-3-(2-naphthyl)propyl nitrate (**21**).* ^{1}H NMR δ 2.10 (1H, m), 2.26 (1H, m), 3.27 (3H, s), 4.43 (1H, m), 4.52 (1H, m), 4.66 (1H, m), 7.44 (1H, d), 7.50 (2H, m), 7.75 (1H, s), 7.85 (3H, d); ^{13}C NMR δ 35.3 (CH_2), 56.8 (CH_3O), 70.2 (CH_2), 79.9 (CH), 123.8 (CH, aromatic), 125.9 (CH, aromatic), 126.1 (CH, aromatic), 126.4 (CH, aromatic), 127.7 (CH, aromatic), 127.8 (CH, aromatic), 128.8 (CH, aromatic), 133.2 (C, aromatic), 138.1 (C, aromatic), 139.5 (C, aromatic); IR ($CHCl_3$) *v* 3018, 1633 (s), 1281, 1216 (s); MS(EI) *m/e* 261 (M^+, 13.6), 171 (M − 90, 100); HRMS(EI) $C_{14}H_{15}O_4N$, calc. 261.1001, exp. 261.0999, error −0.9 ppm.

*b) 1-(2-Naphthyl)propane-1,3-diyl dinitrate (**22**).* ^{1}H NMR δ 2.34 (1H, m), 2.53 (1H, m), 4.47 (1H, m), 4.62 (1H, m), 6.07 (1H, t), 7.47 (1H, d), 7.54 (2H, m), 7.86 (3H, m), 7.91 (1H, d); ^{13}C NMR δ 31.9 (CH_2), 68.4 (CH_2), 81.4 (CH), 123.1 (CH, aromatic), 126.3 (CH, aromatic), 126.9 (CH, aromatic), 127.0 (CH, aromatic), 127.8 (CH, aromatic), 128.1 (CH, aromatic), 129.3 (CH, aromatic), 128.3 (C, aromatic), 133 (C, aromatic), 133.6 (C, aromatic); IR ($CHCl_3$) *v* 3018, 1642, 1281, 1216 (s); MS(EI) *m/e* 292 (M^+, 10.7), 127 (100); HRMS(EI) $C_{13}H_{12}O_6N_2$, calc. 292.0695, exp. 292.0695, error −0.0 ppm.

*c) 3-Hydroxy-3-(2-naphthyl)propyl nitrate (**23**).* ^{1}H NMR δ 2.09 (1H, d, OH), 2.33 (2H, m), 4.57 (1H, m), 4.71 (1H, m), 5.02 (1H, m), 7.82 (4H, m); ^{13}C NMR δ 35.8 (CH_2), 70.2 (CH_2), 72.9 (CH), 123.4 (CH, aromatic), 124.5 (CH, aromatic), 126.2 (CH, aromatic), 126.5 (CH, aromatic), 127.7 (CH, aromatic), 127.9 (CH, aromatic), 128.8 (CH, aromatic), 133.1 (C, aromatic), 133.2 (C, aromatic), 140.6 (C, aromatic); IR ($CHCl_3$) *v* 3605 (-OH), 3018, 1636, 1281, 1215 (s); MS(EI) *m/e* 248 (M + 1, 1.4), 247 (M, 10), 230 (M − OH, 6.5), 157 (M − $CH_2CH_2ONO_2$, 30), 127 (100); HRMS(EI) $C_{13}H_{13}O_4N$, calc. 247.0845, exp. 247.0837, error −3.0 ppm.

CAN oxidation of cyclopropylanthracenes

9-Cyclopropylanthracene (6). 26.6 mg (0.122 mmol) of 9-cyclopropylanthracene was dissolved in 10 mL CH_3CN–CH_3OH (9:1, v/v) and 267.4 mg (0.488 mmol) CAN (mole ratio of CAN to 9-cyclopropylanthracene = 4) was then added. The reaction proceeded immediately. The orange color of the Ce(IV) solution disappeared and instead, a white solid (Ce(III) salt) in the solution was observed. The reaction mixture was stirred under nitrogen at room temperature for 20 minutes and then poured into water and extracted with diethyl ether. The ether layer was dried over $MgSO_4$ and evaporated. Products were separated by PTLC using CH_2Cl_2 as solvent, which yielded 6.5 mg (22%) of 9-cyclopropyl-10-methoxyanthracene,[19] 15.4 mg (48%) of 9-cyclopropyl-9-methoxyanthrone.[19] 21% of anthraquinone and 2% of 9-cyclopropyl-10-hydro-9,10-dimethoxyanthracene were also obtained based on GC analysis.

Another run began with 49.05 mg (0.225 mmol) of 9-cyclopropylanthracene and 274 mg (0.50 mmol) of CAN (mole ratio of CAN to 9-cyclopropylanthracene = 2.2). The reaction proceeded under the same conditions as above and the resulting solution was worked up with H_2O–diethyl ether. PTLC with 3:1 hexane–CH_2Cl_2 as solvent yielded 16.2 mg (29%) of

9-cyclopropyl-10-methoxyanthracene and 5.5 mg (10%) recovered starting material and a mixture of anthraquinone, 9-cyclopropyl-9-methoxyanthrone and 9-cyclopropyl-9-methoxy-10,10-dimethoxyanthracene. A second PTLC of the latter mixture with 5:1 hexane–EtOAc as solvent yielded 5.7 mg (9%) of 9-cyclopropyl-10-hydro-9,10-dimethoxyanthracene, 11.9 mg (17%) of 9-cyclopropyl-9-methoxyanthrone and 4.0 mg (9%) of anthraquinone.

9-Cyclopropyl-10-hydro-9,10-dimethoxyanthracene (27). ^{1}H NMR δ 0.32 (2H, m), 0.73 (2H, m), 1.39 (1H, m), 2.79 (3H, s), 5.13 (3H, s), 7.34 (2H, t), 7.47 (4H, m), 7.65 (2H, d); ^{13}C NMR δ 2.1 (cp-CH_2), 26.5 (cp-CH), 51.5 (OCH_3), 55.9 (OCH_3), 77.3 (C), 78.7 (CH), 126.97 (CH, aromatic), 127.0 (CH, aromatic), 128.4 (CH, aromatic), 129.6 (CH, aromatic), 134.5 (C, aromatic), 141.0 (C, aromatic).

The product distributions for the CAN oxidation of 9-cyclopropylanthracene at various mole ratios of CAN to 9-cyclopropylanthracene were examined as follows: into each of four small vials was placed 5.6 mg (0.0257 mmol) and 1 mL CH_3CN–CH_3OH (9:1, v/v). 13.7 mg (0.025 mmol), 27.4 mg (0.050 mmol), 41.4 mg (0.075 mmol) and 54.8 mg (0.10 mmol) of CAN were added to four vials, respectively. After 20 minutes, the reaction mixtures were worked up with H_2O–diethyl ether, dried over $MgSO_4$, and evaporated. 5 mL CH_3CN was added into each of the vials to dissolve the residue. 0.04 mL of the solution was taken and diluted into 2 mL with CH_3CN. HPLC was employed to analyze the amount of products in each of four samples. The standard solutions of starting material 9-cyclopropylanthracene (0.01 mg mL^{-1}) and major product 9-cyclopropyl-10-methoxyanthracene (0.01 mg mL^{-1}) and 9-cyclopropyl-9-methoxyanthrone (0.04 mg mL^{-1}) in CH_3CN were prepared and HPLC correction factors for these compounds [1.0×10^{-4} (mg mL^{-1})/area, 1.44×10^{-4} (mg mL^{-1})/area and 1.41×10^{-4} (mg mL^{-1})/area, respectively] were determined. The HPLC yields of products thus obtained are summarized in Table 3 (HPLC conditions: CH_3CN–H_2O = 9:1, flow rate = 1 mL min^{-1}, UV detector: λ = 256 nm).

9-Bromo-10-cyclopropylanthracene (7). The reaction of 9-bromo-10-cyclopropylanthracene with CAN was performed by a similar procedure as that for 9-cyclopropylanthracene. In one reaction, 42.2 mg (0.143 mmol) of 9-bromo-10-cyclopropylanthracene and 164.4 mg (0.30 mmol) of CAN were combined in 10 mL 9:1 (v/v) CH_3CN–CH_3OH for 20 min. The resulting solution was worked up and the products were isolated by PTLC with 3:1 hexane–CH_2Cl_2 as solvent, which gave 30.8 mg (60%) of 9-cyclopropyl-9-methoxyanthrone. 9% of anthraquinone was also obtained based on GC analysis.

Another reaction was performed in 1 mL 9:1 (v/v) CH_3CN–CH_3OH containing 6.3 mg (0.021 mmol) of 9-bromo-10-cyclopropylanthracene and 24.7 mg (0.045 mmol) of CAN. The yields of products were determined by HPLC (HPLC conditions: CH_3CN–H_2O = 9:1, flow rate = 1 mL min^{-1}, UV detector: λ = 256 nm). The reaction gave 4.3 mg (76.5%) of *9-cyclopropyl-9-methoxyanthrone (0.01 mg* mL^{-1} standard solution of 9-cyclopropyl-9-methoxyanthrone). 8% of anthraquinone was also obtained based on GC analysis (Table 3).

Acknowledgements

Financial support from the National Science Foundation (CHE-9412814) is acknowledged and appreciated.

References

1 (*a*) R. B. Silverman and S. J. Hoffman, *J. Am. Chem. Soc.*, 1980, **102**, 884; (*b*) R. B. Silverman, S. J. Hoffman and W. B. Catus, III, *J. Am. Chem. Soc.*, 1980, **102**, 7126.
2 (*a*) R. P. Hanzlik and R. H. Tullman, *J. Am. Chem. Soc.*, 1982, **104**, 2048; (*b*) P. Riley and R. P. Hanzlik, *Tetrahedron Lett.*, 1989, **30**, 3015.
3 T. L. Macdonald, K. Zirvi, L. T. Burke, P. Peyman and F. P. Guengerich, *J. Am. Chem. Soc.*, 1982, **104**, 2050.
4 (*a*) A. J. Castellino and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 1313; (*b*) A. J. Castellino and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 7512.
5 J. M. Tanko and R. E. Drumright, *J. Am. Chem. Soc.*, 1990, **112**, 5362.
6 J. M. Tanko and R. E. Drumright, *J. Am. Chem. Soc.*, 1992, **114**, 1844.
7 J. M. Tanko, R. E. Drumright, N. K. Suleman and L. E. Brammer, Jr., *J. Am. Chem. Soc.*, 1994, **116**, 1785.
8 J. M. Tanko, L. E. Brammer, Jr., M. Hervas' and K. Campos, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1407.
9 T. Shono and Y. Matsumura, *J. Org. Chem.*, 1970, **35**, 4157.
10 V. Rao and S. Hixson, *J. Am. Chem. Soc.*, 1979, **101**, 6458.
11 K. Mizuno, K. Yoshioka and Y. Otsuji, *Chem. Lett.*, 1983, 941.
12 L. Young, *Tetrahedron Lett.*, 1968, 5105.
13 R. J. Ouellette and R. J. Bertsch, *J. Org. Chem.*, 1976, **41**, 2782.
14 J. Dinnocenzo, W. Todd, T. Simpson and I. Gould, *J. Am. Chem. Soc.*, 1990, **112**, 2462.
15 J. Dinnocenzo, D. Lieberman, T. Simpson and I. Gould, *J. Am. Chem. Soc.*, 1993, **115**, 366.
16 J. Dinnocenzo, T. Simpson, H. Zuilhof, W. Todd and T. Heinrich, *J. Am. Chem. Soc.*, 1997, **119**, 987.
17 J. Dinnocenzo, H. Zuilhof, D. Lieberman, T. Simpson and M. McKechney, *J. Am. Chem. Soc.*, 1997, **119**, 994.
18 Y. Wang and J. Tanko, *J. Am. Chem. Soc.*, 1997, **119**, 8201.
19 Y. Wang, K. McLean and J. Tanko, *J. Org. Chem.*, 1998, **63**, 628.
20 (*a*) E. Baciocchi, L. Mandolini and C. Rol, *Tetrahedron Lett.*, 1973, 3787; (*b*) E. Baciocchi, L. Mandolini and C. Rol, *Tetrahedron Lett.*, 1976, 3343; (*c*) E. Baciocchi, C. Rol and R. Ruzziconi, *J. Chem. Res.* (*S*), 1984, 334.
21 E. Baciocchi and C. Rol, *J. Am. Chem. Soc.*, 1980, **102**, 7598.
22 (*a*) E. Baciocchi, M. Mattioli, R. Romano and R. Ruzziconi, *J. Org. Chem.*, 1991, **56**, 7154; (*b*) E. Baciocchi, A. Cort, L. Eberson, L. Mandolini and C. Rol, *J. Org. Chem.*, 1986, **51**, 4544.
23 (*a*) E. Baciocchi, T. Giacco and F. Elisei, *J. Am. Chem. Soc.*, 1993, **115**, 12290; (*b*) E. Baciocchi, M. Bietti and M. Mattioli, *J. Org. Chem.*, 1993, **58**, 7106.
24 (*a*) E. Baciocchi, C. Rol and G. Sebastiani, *Gazz. Chim. Ital.*, 1982, **112**, 513; (*b*) E. Baciocchi, M. Bietti, L. Putignani and S. Steenken, *J. Am. Chem. Soc.*, 1996, **118**, 5952.
25 M. Fujita and S. Fukuzumi, *Chem. Lett.*, 1993, 1911.
26 V. Parker, *J. Chem. Soc., Chem. Commun.*, 1968, 610.
27 M. Oyama, K. Nozaki, T. Nagaoka and S. Okazaki, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 33.
28 (*a*) B. Maillard, D. Forrest and K. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7024; (*b*) R. Kinney, R. Jones and R. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 7902; (*c*) A. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1473; (*d*) A. Effio, D. Griller, K. Ingold, A. Beckwith and A. Serelis, *J. Am. Chem. Soc.*, 1980, **102**, 1734; (*e*) L. Mathew and J. Warketin, *J. Am. Chem. Soc.*, 1986, **108**, 7981; (*f*) A. Beckwith, V. Bowry and G. Moad, *J. Org. Chem.*, 1988, **53**, 1632; (*g*) M. Newcomb and A. Glenn, *J. Am. Chem. Soc.*, 1989, **111**, 275; (*h*) A. Beckwith and V. Bowry, *J. Org. Chem.*, 1989, **54**, 2681.
29 D. Tanner, J. Chen, C. Luelo and P. Peters, *J. Am. Chem. Soc.*, 1992, **114**, 713.
30 X. Zhang and F. G. Bordwell, *J. Org. Chem.*, 1992, **57**, 4163.
31 H. Simmons, T. Cairns, S. Vladuchick and C. Hoiness, in *Organic Reactions, Vol. 20*, J. Baldwin, R. Bittman, W. Dauben, J. Fried, R. Heck, A. Kende, W. Leimgruber, J. Marshall, B. McKusick, J. Meinwald, B. Trost and B. Weinstein, eds., John Wiley & Sons, Inc., New York, 1973, pp. 1–132.
32 R. Hahn, P. Howard, S. Kong, G. Lorenzo and N. Miller, *J. Am. Chem. Soc.*, 1969, **91**, 3558.
33 N. Bauld, J. McDermed, C. Hudson, Y. Rim, J. Zoeller, R. Gordon and J. Hyde, *J. Am. Chem. Soc.*, 1969, **91**, 6666.
34 H. Mas Rosemal, *Stereoelectronic effects in the brominations of cyclopropylarenes and 9-alkylanthracenes*, PhD Thesis, 1989, Chapter 5, p. 101, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.
35 This compound has been previously prepared, but not fully characterized. See Yu. S. Shabarov, S. S. Mochalov, N. B. Matreeva and I. P. Stepanova, *Zh. Org. Khim.*, 1975, **11**, 568. See also V. I. Dainenko and Yu. S. Shaparov, *Bull. Acad. Sci. USSR*, 1983, **32**, 1615.

Paper 8/05655B