Tetrahedron 64 (2008) 5666–5671

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Electrophilic aromatic addition reaction (Ad_EAr) to anthracene

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ARTICLE INFO

Article history:
Received 5 April 2008
Accepted 9 April 2008
Available online 11 April 2008

ABSTRACT

After finding in a previous study that naphthalene and quinoline can react via electrophilic aromatic addition reaction (Ad_EAr), we applied this to anthracene. When anthracene was reacted with bromine in methanol in the presence of $NaHCO_3$ and pyridine, 9,10-dihydro-9,10-dimethoxyanthracene (**2**) was obtained in 82% yield in the absence of substitution products or oxidative demethylation products like anthraquinone. The same reaction in ethanol produced 9,10-diethoxy-9,10-dihydroanthracene (**9**) in much lower yield (45%). In addition, we investigated the reactivity of addition product **2**. Treatment of **2** with DDQ in benzene at 65 °C for 12 h produced 9,10-dimethoxyanthracene (**3**) in 62% yield, and **2** was rapidly transformed to 9-methoxyanthracene (**4**) in methanolic NaOH in 10 min. Moreover, the acid-catalyzed aromatization of **2** in 1-propanol at 75 °C for 10 min gave 9-*n*-propoxyanthracene (**8**) in 65% yield.

1. Introduction

During electrophilic aromatic substitution, σ-complex formation is generally the rate determining step as compared with aromatization step by deprotonation.[1] σ-Complexes may proceed via two compatible pathways, i.e., rearomatization[1] or nucleophilic addition.[2] Recently, the transition-metal catalyzed ring openings of oxabenzonorbornadienes[3] and azabenzonorbornadienes[4] by various nucleophiles have provided dihydronaphthalene derivatives, consequently constructing multiple stereocenters. During electrophilic aromatic substitution, if addition of various nucleophile to σ-complex are controlled, it might be possible to generate addition products with two stereocenters. In particular, dihydropolycyclic aromatic hydrocarbon skeletons have been found in a wide range of natural compounds and exhibit a plethora of biological activities.[5] Moreover, when the rearomatization of a σ-complex by deprotonation is blocked, *ipso* attack at a pre-substituted position provides the possibility of nucleophile addition in benzenoid systems.[6] Recently, we described the isolation of addition products in fused systems.[7] The identification of one unusual adduct by X-ray crystallography suggested that electrophilic aromatic addition (Ad_EAr) reaction may provide a useful method of introducing functionalization into fused aromatic systems.

Anthracene and its derivatives have been extensively investigated in many fields, e.g., material chemistry,[8] high fluorescence, thermochromic or photochromic fields,[9] and they have been applied to optical, electronic, and magnetic switches, and incorporated into polymers, films, and crystals.[10] In biological systems, anthracene based compounds are also useful for probing DNA cleavage.[11] Recently, several epoxy-anthracenes and their derivatives have been synthesized by bromination and sequential base treatment.[12]

Generally speaking, the central B-ring of anthracene is considerably more reactive than the other two rings. Moreover, σ-complex at the C9-position of anthracene could be stabilized by the two benzene rings, which might prevent rearomatization.[1a] However, no straightforward efficient method of preparing symmetrical 9,10-dialkoxy-9,10-dihydroanthracene with a trans stereochemistry has been reported in the literature. Here, we describe the Ad_EAr chemistry of anthracene, and of the related compounds, alkoxyanthracene, alkylanthracene, and phenanthrene. In addition, the reactivities of the Ad_EAr adducts were investigated to determine whether they are likely to have applicable utility.

2. Results and discussion

2.1. Ad_EAr reaction of anthracene in methanol

Ad_EAr reaction of anthracene (**1**) under previously reported optimized basic methanolic conditions,[7] produced 9,10-dihydro-9,10-dimethoxyanthracene (**2**), with a trans stereochemistry in high yield (82%, Table 1, entry 2). Reaction of anthracene with 3 equiv of bromine in methanolic $NaHCO_3$ (2.0 equiv) solution in the presence of pyridine at rt provided a new spot by TLC. Initially, we thought that it was 9,10-anthraquinone, because 9,10-dimethoxyanthracene can be oxidized to anthraquinone by either direct oxidation or

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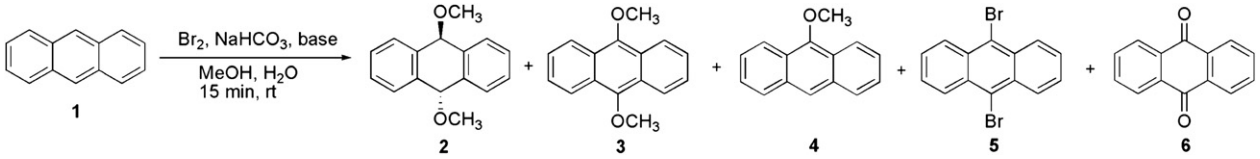
doi:10.1016/j.tet.2008.04.032

Table 1
Effect of amine base on the rate of Ad_EAr reaction of anthracene[a]



Entry	Amine base	Yield of product[b] (%)					
		1	**2**	**3**	**4**	**5**	**6**
1	Urea	—	64	2	3	Trace	—
2	Pyridine	—	82	1	1	Trace	—
3	Imidazole	24	—	4	10	Trace	5
4	DMAP	8	—	8	6	Trace	4
5	DABCO	5	54	2	10	Trace	—
6	DBU	10	—	7	11	Trace	7
7[c]	None	5	—	9	7	Trace	43

[a] All reactions were carried out on the 2.0 mmol of anthracene (**1**) reaction scale using 3.0 equiv of bromine and 2.0 equiv of $NaHCO_3$ with 6.0 mL of MeOH at rt for 15 min.
[b] Isolated yield.
[c] 10-Methoxy-10*H*-anthracene-9-one (**7**) was also obtained in 20% isolated yield.

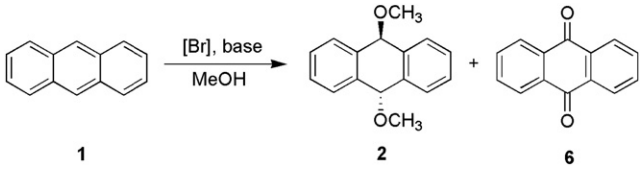
demethylation–oxidation by NBS under acid conditions.[13] However, we obtained Ad_EAr adduct 9,10-dihydro-9,10-dimethoxyanthracene (**2**) instead of anthraquinone. It was reported that an isolated addition adduct of anthracene in the nitration of anthracene could be proceeded either by elimination (giving an anthracene ring) or by remaining adduct intermediate (stabilization by two benzenoid rings).[1a] This is a result of the relatively close balance in resonance stabilization of two different routes. During the nitration of anthracene, the fact that addition takes place in the presence of HCl to produce 9-chloro-9,10-dihydro-10-nitroanthracene could provide an example of an aromatic addition reaction.[14] This result means that it could be possible to control the formation of either the adduct or the substitution product by changing the reaction condition.

In this study, we were also able to selectively rearomatize Ad_EAr adduct using various methods, i.e., oxidation using DDQ, basic-catalyzed elimination in MeOH, acid-catalyzed transetherification using 1-propanol, and introduction of an additional mechanism on the electrophilic substitution reaction. The ^1H NMR spectrum of the isolated new product clearly showed symmetrical peaks at 3.40 ppm (s, 6H), 5.40 ppm (s, 2H) and 7.24–7.40 ppm (m, 4H), 7.55–7.62 ppm (m, 4H). We fully identified this TLC separated adduct as 9,10-dihydro-9,10-dimethoxyanthracene (**2**), which was formed as a result of Ad_EAr. To the best of our knowledge, this is the first reported isolation of a dimethoxy addition, which does not contain bromine, and which has a trans stereochemistry. Rindone and Scolastico reported that the oxidation of anthracene using lead tetraacetate $Pb(OAc)_4$ gave a mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethoxyanthracene.[15] Based on their ^1H NMR analysis, the protons of the cis and trans compounds produced peaks at δ 3.29 (s), 5.25 (s) and 3.39 (s), 5.38 (s) ppm, respectively. As the peaks of **2** prepared by Ad_EAr reaction are at 3.42 (s) and 5.40 (s), respectively, compound **2** has a trans stereochemistry. Small amounts of substitution compounds, such as 9,10-dimethoxyanthracene (**3**) and 9-methoxyanthracene (**4**) were also isolated. In addition, the brominated compound, 9,10-dibromoanthracene (**5**), was present in trace amounts.

To optimize the Ad_EAr reaction of anthracene, we checked the effects of various amine bases, as shown in Table 1. When bromine was added dropwise in the presence of pyridine (entry 2), the yellow color of reaction mixture became red, but when bromine was added in DMAP, the yellow color remained (entry 4). Based on the results shown in Table 1, pyridine was the optimal base for the Ad_EAr reaction of anthracene to produce adduct **2** in high yield (entry 2). On the other hand, amines with high basicity and low steric hindrance around their nucleophilic nitrogens, such as DMAP and DBU (entries 4 and 6), produced no conversion of **2** under the same conditions. However, bromination with DBU in acetic acid improved the yield of **5**.[16] 9,10-Dibromoanthracene was always produced only in trace amounts regardless the reaction conditions. When the moderately hindered weak base DABCO was used, compound **2** was obtained in 54% yield. Interestingly, when we used highly basic amines, such as imidazole, DMAP, or DBU (entries 3, 4, and 6), we obtained the oxidatively demethylated compound, anthraquinone (**6**) instead of **2**. In terms of the Ad_EAr reaction of anthracene without pyridine, anthraquinone (**6**) was obtained in 43% yield with 10-methoxy-10*H*-anthracen-9-one (**7**, 20%) as a by-product (entry 7).

We also examined the effects of bromine sources and inorganic bases on the Ad_EAr reaction of anthracene, as shown in Table 2. To determine the effects of inorganic bases on the Ad_EAr reaction of

Table 2
Ad_EAr reactions of anthracene using different conditions[a]



Entry	Condition	Inorganic base	Yield of product[b] (%)			Others
			1	**2**	**6**	
1	Br_2/Py	*t*-BuOK	23	—	9	**3** (5), **4** (38)
2	Br_2/Py	Cs_2CO_3	22	49	—	—
3	Br_2/Py	K_2CO_3	—	25	—	—
4	Br_2/Py	NaOH	27	—	14	**3** (20), **4** (16)
5	Br_2/Py	NaOMe[c]	23	—	—	**3** (4)
6	Br_2/Py	$NaHCO_3$[d]	—	59	—	—
7	Br_2[e]/Py	$NaHCO_3$	—	52	—	—
8	Br_2[f]/Py	$NaHCO_3$	19	27	—	**4** (6)
9	Py·HBr_3	$NaHCO_3$	5	—	27	**3** (11), **4** (6)
10	NBS/Py	$NaHCO_3$	—	—	—	**4** (48)[g]

[a] All reactions were carried out on the 2.0 mmol of anthracene (**1**) reaction scale using 3.0 equiv of bromine and 2.0 equiv of $NaHCO_3$ with 6.0 mL of MeOH at rt for 15 min.
[b] Isolated yield.
[c] Used in 0.5 M methanol solution.
[d] $NaHCO_3$ was present at 3.0 equiv.
[e] Bromine was used at 2.0 equiv and acetone was used as a solvent for work up.
[f] Bromine was used at 1.0 equiv and acetone was used as a solvent for work up.
[g] Yields were determined based on ^1H NMR findings.

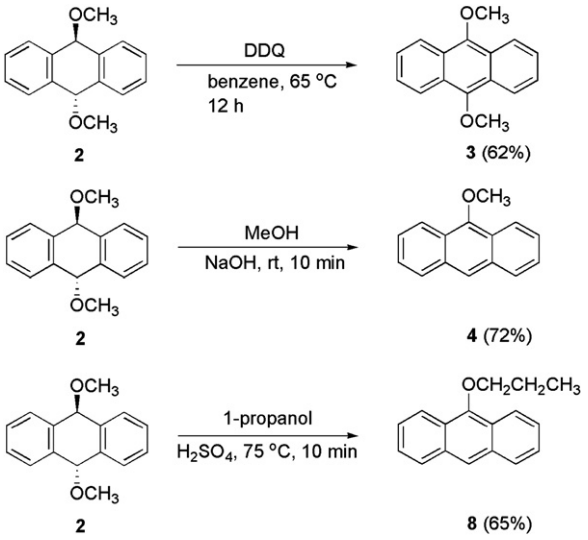
anthracene, we used a range of weak (e.g., alkali metal carbonates) to strong bases. Ad_EAr reaction of **1** under various conditions in the presence of $NaHCO_3$ gave **2** in 59%, 52%, and 82% yields (entries 6 and 7 in Table 2 and entry 2 in Table 1), respectively. On the other hand, Ad_EAr reaction of **1** in the presence of strong bases, such as potassium *tert*-butoxide, sodium hydroxide, or sodium methoxide resulted in little or no adduct **2** formation (entries 1, 4, and 5). Reactions in the presence of alkali metal carbonates, including cesium and potassium carbonates, using the same procedure produced **2** (entries 2 and 3). Thus, it appears likely that the adduct **2** can be preferentially obtained by controlling the amount of weak base used.

Ad_EAr reaction was also carried out using other brominating agents, namely, pyridinium hydrobromide perbromide ($Py\cdot HBr_3$)[17] and NBS (entries 10 and 11). We considered that $Py\cdot HBr_3$ might be a more convenient brominating agent, but it was ineffective (entry 9). When NBS was used, 9-methoxyanthracene (**4**) was only obtained in 48% yield. It has been reported that bromination of anthracene with NBS in CCl_4 afforded 9-bromoanthracene in good yield.[18] Thus, Ad_EAr reaction in the presence of NBS under basic methanolic conditions proceeds in a different manner from bromination with NBS in CCl_4. These results indicate that the base and the bromination reagent are important for obtaining the addition product in high yield. When 3 equiv of $NaHCO_3$ were used, the yield of addition product **2** decreased to 59% (entry 6). Also when we reduced the amount of bromine to 2.0 and 1.0 equiv, we obtained **2** in lower yields of 52 and 27%, respectively (entries 7 and 8).

The selection of the base is a critical factor in this reaction. To find out the key role of pyridine, we have performed the experiments as described in Tables 1 and 2. At this moment, we cannot explain the role of pyridine.

2.2. Reactions of Ad_EAr product 2

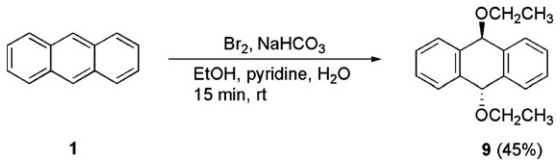
During Ad_EAr reaction of anthracene in methanol, substituted products, such as **3** and **4** were isolated (Scheme 1). The formation of these by-products was thought to provide useful information on the mechanism of Ad_EAr reaction and on the applicabilities of Ad_EAr product **2**.



Scheme 1. Aromatization of the Ad_EAr adduct under various condition.

Product **2** was oxidized by DDQ to produce the rearomatized 9,10-dimethoxyanthracene (**3**) in 62% yield. Product **2** was also selectively rearomatized to 9-methoxyanthracene (**4**) by an elimination reaction in strong basic methanolic solution at rt for 10 min. In addition, an interesting transetherification occurred when product **2** was reacted with 1-propanol under acid-catalyzed (H_2SO_4) conditions at 75 °C for 10 min. Moreover, the transetherification product, 9-*n*-propoxyanthracene (**8**, 65%), was obtained with 9-methoxyanthracene (**4**, 15%) and anthracene (**1**, trace amount) as minor products.

When EtOH was used instead of MeOH using the same reaction conditions, a new adduct 9,10-diethoxy-9,10-dihydro-anthracene (**9**) was obtained as a white solid with trans stereochemistry. This product did not contain bromine as was expected, but its yield was lower than that in methanol (Scheme 2).



Scheme 2. Ad_EAr reaction to anthracene (**1**) in EtOH.

2.3. Ad_EAr reaction of other anthracene derivatives

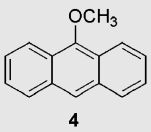
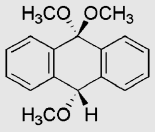
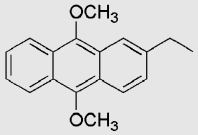
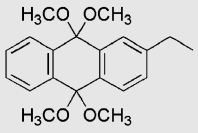
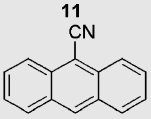
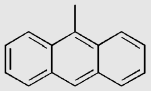
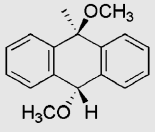
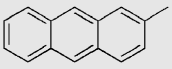
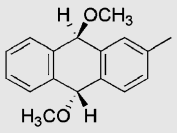
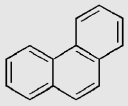
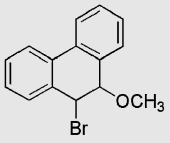
As shown in Table 3, Ad_EAr reactions of 9-methoxy-, 9,10-dimethoxy-2-ethyl-, 9-cyano-, 2-methyl-, and 9-methylanthracene derivatives were carried out at the same reaction conditions. 9-Methoxyanthracene (**4**) readily underwent Ad_EAr reaction to provide the new addition product 9,10-dihydro-9,9,10-trimethoxyanthracene (**10**) in high yield (92%, entry 1). Moreover, the dimethoxy derivative, 9,10-dimethoxy-2-ethylanthracene (**11**), produced the new addition product 2-ethyl-9,9,10,10-tetramethoxyanthracene (**12**) in 70% of yield, which was formed via the same mechanism as anthracene (**1**) and 9-methoxyanthracene (**4**). Ad_EAr reactions of 9-methylanthracene (**14**) and 2-methylanthracene (**16**) also produced new adducts in high yields (entries 4 and 5). However, in the case of 9-cyanoanthracene (**13**), which has a strong electron withdrawing group, Ad_EAr reaction did not occur (entry 3). When Ad_EAr reaction was applied to phenanthrene (another tricyclic aromatic compound, entry 6), we obtained a different addition product, 9-bromo-10-methoxy-9,10-dihydrophenanthrene (**19**). We attribute the formation of different addition product to the different reactivities of phenanthrene and anthracene.

2.4. Proposed mechanism

A suggested mechanism of the Ad_EAr reaction of anthracene (**1**) is shown in Scheme 3. First, bromination at the 9-position of anthracene occurs, and the brominated cation formed is stabilized by methoxide addition. The finding that 9,10-dibromoanthracene (**5**) was obtained in trace amounts suggests that methoxide reacts more rapidly than bromide at the 10-position of the brominated cation. Thus, attack by methoxide may be an important step in the formation of 9,10-dihydro-9,10-dimethoxyanthracene (**2**).

Methoxide then attacks the bromo group at the benzylic position of the 9-bromo-9,10-dihydro-10-methoxyanthracene intermediate either in an S_N1 or S_N2 manner to produce 9,10-dihydro-9,10-dimethoxyanthracene (**2**). 9-Methoxyanthracene (**4**) was obtained as a by-product via the dehydrobromination of 9-bromo-9,10-dihydro-10-methoxyanthracene intermediate. We believe that 9,10-dimethoxyanthracene (**3**) might be formed by oxidation in air. Further bromination and methoxide addition to 9-methoxyanthracene (**4**) might have produced the new adduct 9,10-dihydro-9,9,10-trimethoxyanthracene (**10**) via a repetition of the same process.

Table 3
Ad_EAr reaction of various aromatic compounds under methanolic $NaHCO_3$ conditions[a]

Entry	Aromatics	Product	Yield[b] (%)
1	 **4**	 **10**	92
2	 **11**	 **12**	70
3	 **13**	—	No Rx
4	 **14**	 **15**	79
5	 **16**	 **17**	77
6	 **18**	 **19**	22

[a] All reactions were carried out using 2.0 mmol of each material under the same conditions.
[b] Isolated yield.

3. Conclusion

The present study demonstrates that Ad_EAr reaction could provide a useful means for preparing various anthracene derivatives. Treatment of anthracene with bromine in alcoholic (MeOH, EtOH)–$NaHCO_3$ afforded the corresponding addition product 9,10-dialkoxy-9,10-dihydroanthracene in excellent yield at high purity with a trans stereochemistry. The selective rearomatizations of the addition product **2** to 9,10-dimethoxyanthracene (**3**) and 9-methoxyanthracene (**4**) were achieved by DDQ oxidation in the former and by methanol elimination under basic conditions in the latter. Transetherification of **2** with 1-propanol under acid-catalyzed (H_2SO_4) conditions formed 9-*n*-propoxyanthracene (**8**) in moderate yield (65%). Further studies on the use of transetherification to make 9-anthryl ethers under acid conditions are in progress.

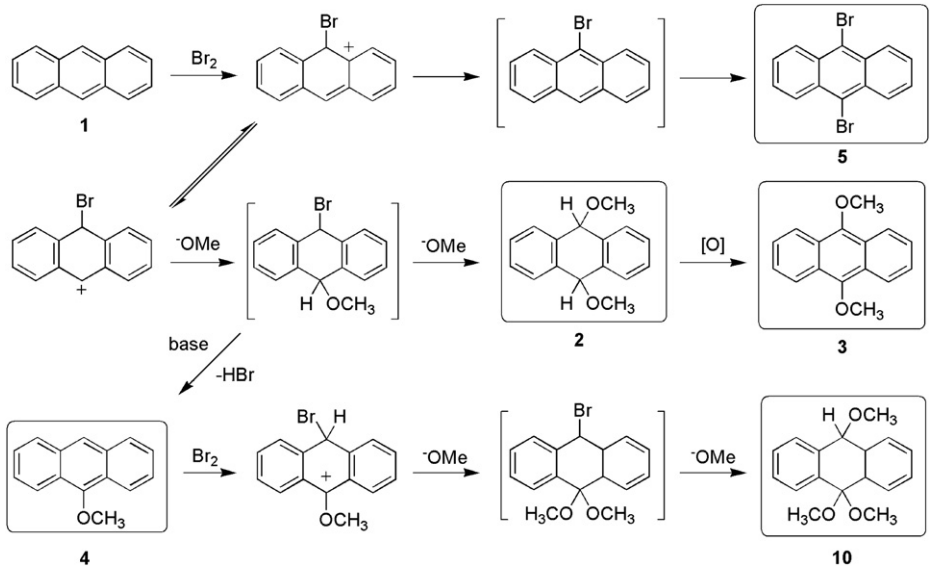
4. Experimental

4.1. Typical procedure used for electrophilic aromatic addition (Ad_EAr) reaction

Sodium bicarbonate (336 mg, 4.0 mmol) was added to solution of anthracene (356 mg, 2.0 mmol) in MeOH (6.0 mL) with stirring for 3 min at rt. Pyridine (165 μL, 2.0 mmol) was added, and 2 min later a solution of Br_2 (307 μL, 6.0 mmol) in MeOH (1.5 mL) was added dropwise. The reaction mixture was then stirred at rt for 10 min. Water (3.0 mL) was then added, the reaction was stirred for another 15 min, and then H_2O (30 mL) and Na_2SO_3 (0.32 g) were added. The mixture was extracted with CH_2Cl_2 (20 mL×2) and the combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The purification of the residue by flash column chromatography (2% EtOAc/hexane) yielded *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**2**, 265 mg, 82%) as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (s, 6H), 5.40 (s, 2H), 7.24–7.40 (m, 4H), 7.55–7.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.6, 77.9, 126.8, 127.5, 137.2; MS (EI) 240 (M^+), 225, 208 (100), 193, 178, 165, 152, 151, 139, 104. HRMS (EI) calcd for $C_{16}H_{16}O_2$ (M^+) 240.1150, found 240.1147.

4.2. 9,10-Dimethoxyanthracene (3)

Yellow solid; mp 196.5–196.6 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.13 (s, 6H), 7.48–7.53 (m, 4H), 8.28–8.33 (m, 4H); ^{13}C NMR



Scheme 3. Suggested mechanism of A_EAr reaction of anthracene.

(100 MHz, $CDCl_3$) δ 63.2, 122.5, 124.8, 125.3, 148.4; MS (EI) 238 (M^+), 223 (100), 208, 180, 152, 125, 111. HRMS (EI) calcd for $C_{16}H_{14}O_2$ (M^+) 238.0994, found 238.1000. Registry No. 2395-97-3. *Procedure for the DDQ oxidation of trans-9,10-dihydro-9,10-dimethoxyanthracene*: DDQ (340 mg, 1.5 mmol) was added to a solution of *trans*-9,10-dihydro-9,10-dimethoxyanthracene (120 mg, 0.5 mmol) in benzene (5 mL), and the mixture was heated at 65 °C for 12 h. The mixture obtained was concentrated and filtered to remove insoluble material, the filtrate was extracted with EtOAc (10 mL×3). Combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by flash column chromatography (10% EtOAc/hexane) yielded 9,10-dimethoxyanthracene (**3**, 74 mg, 62%) as a yellow solid.

4.3. 9-Methoxyanthracene (4)

Pale yellow solid; mp 93.2–93.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (s, 3H), 7.46–7.51 (m, 4H), 7.99 (dd, J=7.2, 2.0 Hz, 2H), 8.23 (s, 1H), 8.30 (d, J=6.8 Hz, 1H), 8.31 (d, J=1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.2, 122.2, 122.3, 124.4, 125.2, 125.5, 128.4, 132.4, 152.2; MS (EI) 208 (M^+), 193 (100), 176, 165, 163, 139, 115, 104. HRMS (EI) calcd for $C_{15}H_{16}O$ (M^+) 208.0888, found 208.0890. Registry No. 2395-96-2. *Procedure for the treatment of trans-9,10-dihydro-9,10-dimethoxyanthracene with methanolic NaOH*: A solution of *trans*-9,10-dihydro-9,10-dimethoxyanthracene (120 mg, 0.5 mmol) in NaOH methanol solution (5 mL) was stirred at rt for 10 min. The mixture was then concentrated and the residue extracted with EtOAc (10 mL×3). Combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by flash column chromatography (10% EtOAc/hexane) yielded 9-methoxyanthracene (**4**, 75 mg, 72%) as a yellow solid.

4.4. 9,10-Dibromoanthracene (5)

Yellow solid; mp 211.8–213.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.65 (m, 4H), 8.58–8.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.5, 127.5, 128.3, 131.1; MS (EI) 338 (M^+), 336 (M^+), 334 (M^+), 295, 279, 240, 208 (100), 178, 165, 152, 139. HRMS (EI) calcd for $C_{14}H_8Br_2$ (M^+) 333.8993, found 333.8989. Registry No. 523-27-3.

4.5. Anthraquinone (6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.81 (m, 4H), 8.30–8.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 133.5, 134.1, 183.2; MS (EI) 208 (M^+, 100), 180, 152, 126. HRMS (EI) calcd for $C_{14}H_8O_2$ (M^+) 208.0524, found 208.0524. Registry No. 84-65-1.

4.6. 10-Methoxy-10*H*-anthracen-9-one (7)

Yellow solid; mp 99.6–99.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (s, 3H), 5.81 (s, 1H), 7.52–7.56 (m, 2H), 7.68–7.72 (m, 2H), 7.79–7.81 (m, 2H), 8.33 (dd, J=8.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 72.3, 127.6, 128.7, 128.9, 132.7, 133.7, 140.4, 183.6; MS (EI) 224 (M^+), 209, 193 (100), 180, 165, 152, 139, 115, 105. HRMS (EI) calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0842. Registry No. 14629-83-5.

4.7. *trans*-9,10-Diethoxy-9,10-dihydroanthracene (9)

White solid; mp 46.6–46.9 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (t, J=7.0 Hz, 3H), 3.70 (q, J=7.0 Hz, 4H), 5.49 (s, 2H), 7.31–7.39 (m, 4H), 7.57–7.65 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.4, 65.0, 77.0, 126.6, 127.4, 138.1; MS (EI) 268 (M^+), 240, 212 (100), 193, 178, 165, 152, 151, 139, 104. HRMS (EI) calcd for $C_{18}H_{20}O_2$ (M^+) 248.1463, found 248.1458.

4.8. 9,10-Dihydro-9,9,10-trimethoxyanthracene (10)

Pale yellow solid; mp 45.1–45.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 3H), 3.11 (s, 3H), 3.17 (s, 3H), 5.50 (s, 1H), 7.45–7.47 (m, 4H), 7.67–7.69 (m, 2H), 7.77–7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 52.2, 53.5, 74.0, 98.7 126.8, 127.4, 128.0, 128.8, 134.7, 137.4; MS (EI) 269 (M^+), 255, 239, 238, 208, 193 (100), 180, 165, 152, 139, 104. HRMS (EI) calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, found 270.1253.

4.9. 2-Ethyl-9,9,10,10-tetramethoxyanthracene (12)

White solid; mp 48.3–48.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J=7.6 Hz, 3H), 2.77 (q, J=7.6 Hz, 2H), 2.96 (s, 12H), 7.37 (dd, J=8.4, 1.2 Hz, 1H), 7.51–7.54 (m, 2H), 7.63 (s, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.79–7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 56.9, 81.4, 124.3, 124.5, 127.9, 128.4, 129.8, 129.9, 131.0, 131.2, 132.3, 132.4, 133.4; MS (EI) 328 (M^+), 297 (100), 266, 251, 223, 193, 165, 152, 133. HRMS (EI) calcd for $C_{20}H_{24}O_4$ (M^+) 328.1675, found 328.1667.

4.10. 9,10-Dihydro-9,10-dimethoxy-9-methylanthracene (15)

Yellow solid; mp 55.3–55.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.83 (s, 3H), 3.23 (s, 3H), 5.23 (s, 1H), 7.37–7.39 (t, J=7.2 Hz, 2H), 7.74 (d, J=6.4 Hz, 1H), 7.75 (d, J=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.6, 51.8, 54.9, 77.1, 78.0, 126.1, 127.1, 128.7, 129.4, 134.2, 141.7; MS (EI) 254 (M^+), 239, 222 (100), 207, 193, 178, 165, 152. HRMS (EI) calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, found 254.1317.

4.11. 9,10-Dihydro-9,10-dimethoxy-2-methylanthracene (17)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.35 (s, 3H), 3.41 (s, 3H), 5.35 (s, 1H), 5.38 (s, 1H), 7.15 (d, J=7.6 Hz, 1H), 7.32–7.34 (m, 2H), 7.41 (s, 1H), 7.45 (d, J=8.0 Hz, 1H), 7.55–7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 56.1, 56.5, 77.7, 126.7, 127.0, 127.3, 127.46, 127.50, 128.2, 134.0, 137.23, 137.30, 137.35, 137.5; MS (EI) 254, 239, 222 (100), 207, 192, 178, 165, 152. HRMS (EI) calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, found 254.1312.

4.12. 9-Bromo-9,10-dihydro-10-methoxyphenanthrene (19)

Greenish solid; mp 88.6–88.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (s, 3H), 4.55 (d, J=2.4 Hz, 1H), 5.45 (d, J=2.8 Hz, 1H), 7.32–7.52 (m, 6H), 7.87–7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 56.9, 81.4, 124.3, 124.5, 127.9, 128.4, 129.8, 129.9, 131.0, 131.2, 132.3, 132.4, 133.4; MS (EI) 290 (M^+), 288 (M^+), 286 (M^+), 272, 243, 223, 208, 194, 178 (100), 165, 151, 139, 104. HRMS (EI) calcd for $C_{15}H_{13}BrO$ (M^+) 288.0150, found 288.0141.

4.13. 9-*n*-Propoxyanthracene (8)

A catalytic amount of sulfuric acid (2.0 μL) was added to a solution of *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**2**, 120 mg, 0.5 mmol) in 1-propanol (2.0 mL). The mixture was then heated at 75 °C for 10 min. After cooling to rt, the mixture was extracted with ethyl acetate (10 mL×3) and water (10 mL). Combined organic layers were then washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by flash column chromatography gave **8** (30% CH_2Cl_2/hexane) as a white solid: mp 75.5–77.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J=7.4 Hz, 3H), 2.07–2.12 (m, 2H), 4.18 (t, J=6.8 Hz, 2H), 7.45–7.50 (m, 4H), 7.98–8.01 (m, 2H), 8.22 (s, 1H), 8.30–8.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.7, 23.9, 77.6, 121.9, 122.4, 124.7, 125.0, 125.4, 128.4, 132.4,

151.4; MS (EI) 236 (M^+), 194 (100), 165, 139. HRMS (EI) calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1204. Registry No. 92830-42-7.

Acknowledgements

This work was supported by an Inha University Research Grant (Inha-2007). High resolution mass spectra were carried out at the Korea Basic Science Institute (Daegu, Korea).

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.04.032.

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