A New Convenient Synthesis of Alkoxyanthracenes from Alkoxy-9,10-anthraquinones

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Abstract: Methoxy-9,10-anthraquinones with mono-, di- and tetraether groups at different positions **1a–h** can be directly reduced to the corresponding methoxyanthracenes **3a–h** in moderate to good yields by zinc in refluxing acetic acid. Under similar conditions, ethyl 1'-anthracenoxyacetate (**3i**) with the ester group unaffected and 1,8-oxybis(ethyleneoxyethyleneoxy)anthracene (**5**) were also conveniently synthesized in 65 and 70% yields, respectively.

Key words: reduction, alkoxy-9,10-anthraquinones, alkoxyanthracene, zinc

Alkoxyanthracenes have attracted considerable interest due to their photochromic properties for the construction of photoresponsive supramolecular systems¹ and on account of their unique chemical reactive properties for the synthesis of triptycenes and triptycene quinones.² The reductive aromatization of the related alkoxy-9,10-anthraquinones provides the most effective route to some alkoxyanthracenes, but the proper reductive system must be selected.³ The reduction reaction can usually be achieved by either excess sodium borohydride⁴ or complicated sodium borohydride-metal (Na or Li)-ammonia/pchloranil system⁵ in a stepwise procedure. Although onestep reductive system of zinc/aqueous ammonia,⁶ zinc/ aqueous sodium hydroxide⁷ or zinc/cyclohexyl-p-toluenesulfonate/hot trichlorobenzene⁸ are sometimes possible, they are often unreliable or of limited substrate and preparative value. Herein we report a new convenient method to alkoxyanthracenes.

In the course of our studies on the construction of novel macrocyclic compounds and new supramolecular systems, we needed 1,8-dimethoxy-9,10-dihydroanthracene (2) and some alkoxyanthracenes including 1,8-dimethoxyanthracene (3a) as starting materials. After examining the literature, we followed Müller's procedure⁹ in which 1,8-dimethoxy-9,10-anthraquinone (1a) was reduced by zinc in refluxing acetic acid for 30 hours to give the corresponding 1,8-dimethoxy-9,10-dihydroan-thracene (2). Compound 2 can then be oxidized to 1,8-dimethoxyanthracene 3a by *p*-chloranil⁵ (Scheme 1).

We found that when **1a** was treated with zinc in refluxing acetic acid for about 16 hours, the TLC showed the disappearance of the starting material **1a** and the formation



Scheme 1

of a major new product. After work-up of the reaction, to our surprise, we only obtained 1,8-dimethoxyanthracene (**3a**) instead of 1,8-dimethoxy-9,10-dihydroanthracene (**2**) in 75% yield. In the ¹H NMR spectrum of the compound **3a**, the protons of H-9 and H-10 are positioned at 9.24 and 8.36 ppm, respectively. This result encouraged us to examine the zinc/acetic acid system for the reduction of other methoxy-9,10-anthraquinones **1b–h**. After carrying out the reaction for 12–24 hours and monitoring the reaction by TLC for completion, the reactions were quenched with ice water. As expected, the corresponding methoxyanthracenes **3b–h** as the final products were selectively formed and were separated by column chromatography over silica gel in moderate to good yields (Scheme 2, Tables 1 and 2).





As shown in Scheme 2, methoxy-9,10-anthraquinones with mono-, di- and tetraether groups at different positions could be directly reduced to the corresponding methoxyanthracenes. Furthermore, the acidic reductive system does not cleave the ether group present in the various 9,10-anthraquinones.⁶ Under the same condition, ethyl 1'- anthracenoxyacetate (**3i**) could be selectively obtained from the reduction of the related 9,10-anthraquinone derivative **1i** without affecting the ester group in **1i**.

We have also found that 1,8-oxybis(ethyleneoxyethyleneoxy)-9,10-anthraquinone (4),¹⁴ prepared from the reac-

SYNTHESIS 2003, No. 16, pp 2464–2466 Advanced online publication: 29.09.2003 DOI: 10.1055/s-2003-42408; Art ID: F05603SS © Georg Thieme Verlag Stuttgart · New York

1, 3	\mathbb{R}^1	R ²	R ³	\mathbb{R}^4	R ⁵	\mathbb{R}^6
b	OMe	Н	Н	Н	Н	Н
c	Н	OMe	Н	Н	Н	Н
d	OMe	Н	OMe	Н	Н	Н
e	OMe	Н	Н	OMe	Н	Н
f	Н	OMe	Н	Н	OMe	Н
g	OMe	OMe	Н	OMe	Н	OMe
h	OMe	Н	OMe	OMe	Н	OMe
i	OCH ₂ CO ₂ Et	Н	Н	Н	Н	Н

Table 1Substituents in Compounds 1 and 3 (see Scheme 2)

tion of 1,8-dichloro-9,10-anthraquinone with tetraethylene glycol in anhydrous THF in the presence of sodium hydride, could be easily reduced by zinc in refluxing acetic acid to afford the 1,8-oxybis(ethyleneoxyethyleneoxy)anthracene (**5**) in good yield (Scheme 3). In the ¹H NMR spectrum, the compound **5** showed two singlets at 9.39 and 8.30 ppm for H-9 and H-10, respectively.



Scheme 3

 Table 2
 Alkoxyanthracenes 3 and Compound 5 Prepared

Sub- strate	Prod- uct	Time (h	Yield (%)	mp (°C) ^a	Lit. mp (°C) or Molecular Formula ^b	¹ H NMR (CDCl ₃) ^c δ , J (Hz
1 a	3a	16	75	195–196	197 ⁵	9.24 (s, 1 H), 8.32 (s, 1 H), 7.57 (d, <i>J</i> = 8.50, 2 H), 7.38 (dd, <i>J</i> = 8.50, 7.47, 2 H), 6.74 (d, <i>J</i> = 7.47, 2 H), 4.09 (s, 6 H, OCH ₃)
1b	3b	12	75	70–71	70–72 ¹⁰	8.86 (s, 1 H), 8.39 (s, 1 H), 8.05–8.08 (m, 1 H), 7.99–8.02 (m, 1 H), 7.60 (d, $J = 8.56$, 1 H), 7.45–7.50 (m, 2 H), 7.39 (dd, $J = 8.56$, 7.37, 1 H), 6.76 (d, $J = 7.37$, 1 H), 4.11 (s, 3 H, OCH ₃)
1c	3c	12	71	183–184	183.1–183.6 ¹¹	8.36 (s, 1 H), 8.29 (s, 1 H), 7.94–7.99 (m, 2 H), 7.90 (d, $J = 9.11, 1$ H), 7.41–7.46 (m, 2 H), 7.21 (s, 1 H), 7.18 (d, $J = 9.11, 1$ H), 3.98 (s, 3 H, OCH ₃)
1d	3d	15	62	134–136	134-136 ^{4a}	8.79 (s, 2 H), 8.03–8.07 (m, 2 H), 7.47–7.50 (m, 2 H), 6.62 (s, 2 H), 4.04 (s, 6 H, OCH ₃)
1e	3e	12	70	227–228	2288	8.80 (s, 2 H), 7.65 (d, <i>J</i> = 8.54, 2 H), 7.37 (dd, <i>J</i> = 8.54, 7.39, 2 H), 6.77 (d, <i>J</i> = 7.39, 2 H), 4.09 (s, 6 H, OCH ₃)
1f	3f	24	60	261–262	260-2625	8.23 (s, 2 H), 7.56 (d, J = 8.96, 2 H), 7.20 (s, 2 H), 7.17 (d, J = 8.96, 2 H), 4.09 (s, 6 H, OCH ₃)
1g	3g	24	50	297–299	298-30012	9.12 (s, 2 H), 6.65 (s, 4 H), 4.05 (s, 12 H, OCH ₃)
1h	3h	24	52	128–130	$C_{18}H_{18}O_4$ (298.12)	9.00 (s, 1 H), 8.74 (s, 1 H), 7.83 (d, $J = 9.15$, 1 H), 7.38 (d, $J = 9.15$, 1 H), 6.60 (ABq, 2 H), 4.11(s, 3 H, OCH ₃), 4.06 (s, 6 H, OCH ₃), 4.04 (s, 3 H, OCH ₃) ^d
1i	3i	6	65	oil	C ₁₈ H ₁₆ O ₃ (280.11)	8.99 (s, 1 H), 8.40 (s, 1 H), 8.10–8.13 (m, 1 H), 8.00–8.03 (m, 1 H), 7.67 (d, $J = 8.57$, 1 H), 7.48–7.54 (m, 2 H), 7.35 (dd, $J = 8.57$, 7.38, 1 H), 6.66 (d, $J = 7.38$, 1 H), 4.90 (s, 2 H), 4.37 (q, $J = 7.13$, 2 H), 1.35 (t, $J = 7.13$, 3 H) ^d
4	5	7	70	157–158	C ₂₂ H ₂₄ O ₅ (368.37)	9.39 (s, 1 H), 8.30 (s, 1 H), 7.56 (d, <i>J</i> = 8.56, 2 H), 7.35 (dd, <i>J</i> = 8.56, 7.34, 2 H), 6.69 (d, <i>J</i> = 7.34, 2 H), 4.36 (t, <i>J</i> = 3.79, 4 H), 4.16 (t, <i>J</i> = 3.79, 4 H) 3.88–3.95 (m, 8 H) ^d

^a Uncorrected.

^b Satisfactory microanalyses obtained: $C \pm 0.17$, $H \pm 0.11$.

^c Recorded on Bruker AM-300 spectrometer.

 ${}^{d 13}C NMR (CDCl_3)^{c}:$ **3h** $: \delta = 55.5, 57.1, 61.1, 100.2, 100.9, 114.0, 116.7, 120.8, 124.3, 125.1, 125.6, 127.5, 128.5, 142.4, 147.0, 149.3, 149.4; \\ \textbf{3i}: \delta = 14.1, 61.4, 65.6, 102.7, 121.3, 121.6, 124.7, 125.2, 125.6, 125.7, 127.8, 128.8, 131.3, 132.0, 132.5, 153.6, 168.8; \textbf{5}: \delta = 68.6, 69.2, 70.2, 71.4, 102.2, 116.4, 120.4, 124.5, 125.0, 125.6, 132.9, 155.1.$

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In conclusion, a new convenient method to prepare alkoxyanthracenes with the ether group at different position has been presented and it may be generally applicable in the synthesis of alkoxyanthracenes.

Methoxy-9, 10-anthraquinones **1a–h** were prepared from the corresponding available hydroxyl-substituted 9,10-anthraquinones and dimethyl sulfate in anhyd acetone in the presence of anhyd K_2CO_3 .¹³ Similarly, compound **1i** was prepared in 85% yield from 1-hydroxy-9,10-anthraquinone and ethyl bromoacetate. 1,8-Oxy-bis(ethyleneoxy)-9,10-anthraquinone (**4**) was prepared from 1,8-dichloro-9,10-anthraquinone and tetraethylene glycol in anhyd THF in the presence of NaH according to the literature.¹⁴

Reduction of Alkoxy-9,10-anthraquinones 1 and 1,8-Oxybis-(ethyleneoxyethyleneoxy)-9,10-anthraquinone (4); General Procedure

To a suspension of 1 or 4 (1.0 mmol) in glacial AcOH (30 mL) was added zinc dust (1.7 g, 26 mmol) in one portion. The reaction mixture was refluxed for 6–24 h. After the reaction was complete (monitored by TLC), the mixture was poured into ice water and extracted with CH_2Cl_2 . The combined organic phase was washed with H_2O and sat. aq solution of NaHCO₃, respectively, and then dried (Na₂SO₄). After removal of the solvent in vacuo, the residue was separated by column chromatography over silica gel to afford the corresponding alkoxyanthracene **3** or 1,8-oxybis(ethyleneoxyethyleneoxy)-9,10-anthracene (**5**) (Tables 1 and 2).

Acknowledgment

This work was supported by the Chinese Academy of Sciences and the National Natural Foundation of China.

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