Anodic Oxidation of Methoxynaphthalenes. Convenient Routes to Methoxylated Naphthalenes and 1,4- and 1,2-Naphthoquinone Mono- and Bis-acetals

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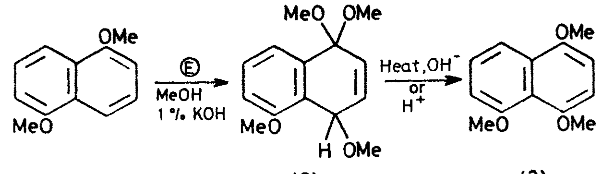
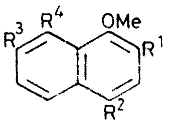
Summary Electrochemical oxidation of naphthalene derivatives often serves as a convenient route to methoxylated naphthalenes and 1,2-naphthoquinone monoacetals.

Anodic oxidation is potentially an excellent procedure for direct introduction of oxygen functionalities into aromatic rings.[1] This reaction, which has been extensively studied in benzenoid systems, is often complicated by overoxidation of the aromatic compound.[2] This is especially important in anodic substitution reactions involving replacement of hydrogen by alkoxy groups since introduction of the oxygen substituent decreases the oxidation potential of the system. The anodic oxidation of naphthalene systems has not been extensively studied[3] and the clean methoxylation noted for 1,5-dimethoxynaphthalene (**1**) prompted further studies in this area.[4] A key feature in the chemistry of (**1**) is that oxidative addition occurs, not oxidative substitution.[5] The intermediate (**2**) is then more difficult to oxidize than (**1**) and the reaction is easily controlled to afford two-electron oxidation products cleanly. We have studied a number of other naphthalene derivatives and note here the results of these studies.

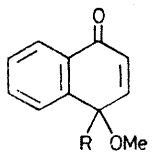


(1) (2) (3)

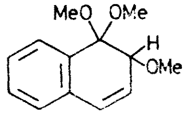
The anodic oxidation of the compounds shown in the Table was conducted in methanol–1% KOH at platinum in a single cell apparatus at 20 °C,[6] the reaction being terminated when the u.v. absorption characteristic of the starting compound stopped decreasing. Current efficiencies were determined by electronic integration. The products isolated after appropriate work up are given in the Table. The structures of compounds (**4**), (**5**), and (**8**) were assigned by comparison with authentic samples. The acetal (**10**) showed the expected spectroscopic properties (i.r. and n.m.r.) and was converted into (**5**) on chromatography (neutral alumina). The structures of the monoacetals (**11**) and (**12**) were assigned on the basis of the similarity of their u.v. spectra with those of analogous chromophores[7] and confirmed by chemical conversion into known compounds. Thus, reduction of (**11**) with sodium borohydride followed by elimination of methanol afforded the known 2-hydroxy-1-methoxynaphthalene.[7a] When (**12**) was reduced with zinc–copper couple and then methylated, the known 1,2,7-trimethoxynaphthalene was obtained.[8] Compound (**7**) was identical to the material obtained by treatment of 5-chloro-7,8-dimethoxy-1-tetralone[9] with Pd–C in cymene followed by methylation with dimethyl sulphate. The ketone (**9**) was reduced with sodium borohydride and methanol was eliminated to afford the known 4-methyl-1-naphthol[10] while (**14**) and (**15**) had physical and spectral properties in agreement with the literature.[11]



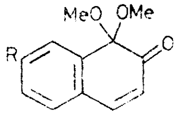
	R^1	R^2	R^3	R^4
(4)	H	OMe	H	H
(5)	OMe	H	H	H
(6)	H	OMe	OMe	H
(7)	OMe	H	H	OMe



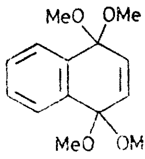
(8) R = OMe
(9) R = Me



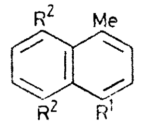
(10)



(11) R = H
(12) R = OMe



(13)



(14) R^1 = H, R^2 = OMe
(15) R^1 = OMe, R^2 = H

Table. Anodic oxidations of naphthalenes (see ref. 6)

Entry	Work up	Naphthalene	Current efficiency/%[a]	Products (%)
1	A	1-OMe	89	(**4**), (**8**), and (**10**)[f] (66, 20, and 8)
2	B	2-OMe	73	(**11**)[f] and (**5**) (35 and 25)
3	B	1,2-di-OMe (**5**)	73	(**11**) (71)
4[3b]		1,4-di-OMe (**4**)	35	(**13**) (74)
5[4]		1,5-di-OMe (**1**)	—	(**3**) (85)
6	C	1,7-di-OMe	47	(**6**)[b] and (**7**)[c] (52 and 21)
7[d]	D	2,7-di-OMe	65	(**12**)[e] (42)
8[d]	E	1-Me	24	(**9**)[f], (**14**), and (**15**) (28, 18, and 16)

Work up procedures were as follows: A, 60 °C, 10 min, silica gel chromatography; B, 2% oxalic acid–tetrahydrofuran (1 : 5), room temp., 1 h, neutral alumina, chromatography; C, 1 equiv. CF_3CO_2H in ether, 0 °C, 2 h,silica gel chromatography; D, 2% acetic acid–acetone (1 : 5), room temp., 3 h, silica gel chromatography; E, 1 equiv. CF_3CO_2H in ether, room temp., 18 h, silica gel chromatography.
[a] Current efficiency for complete disappearance of starting material corrected for four-electron processes. [b] M.p. 43—44 °C. [c] M.p. 52—53 °C. [d] Several unidentified minor products were formed. [e] M.p. 77·5—78·5 °C. [f] Liquid.

These results illustrate several main points. First, anodic addition of methanol is a major pathway in naphthalene systems (entries 1 and 3—6). Thus, in these systems clean two-electron oxidations prevail presumably owing to the stability of dihydronaphthalene intermediates [*i.e.*, (**2**)] under the electrolysis conditions. Second, the α-methoxy groups direct methanol addition predominantly in the 1,4-sense (entries 1 and 4—6) resulting in methoxylation *para* to the original methoxy group after elimination of methanol. Third, β-methoxy substituents afford 1,2-addition products (or alternatively, an anodic substitution at the α-position) which undergo some elimination under the electrolysis conditions to afford 1,2-naphthoquinone bisacetals and subsequently the indicated monoacetals on work up (entries 2, 3, and 7). Unfortunately, in a less activated system (entry 8) much more complex product mixtures result. Finally, the utility of the anodic methoxylation is appropriately illustrated by a reaction sequence involving anodic oxidation of β-methoxynaphthalene, work up (see Table), sodium borohydride reduction, and dimethyl sulphate methylation to afford, without isolation of intermediates, a 58% yield on distillation of 1,2-dimethoxynaphthalene on a *ca.* 0·1 mol scale.

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