Anodic Oxidation of α–naphthol Derivative
A Facile Route to Ring Closure Products.

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Summary: The anodic oxidation of α-naphthol derivatives lead to the formation of naphthoxenium-ion which in the absence of another nucleophile adds to the carboxyl group attached to the side chain in the 4-position. In fact the ring closure product depends on the side chain length and the group attached to the side chain.

Introduction

Many biosynthetic processes are known to pass through quinonoid intermediates. The literature on the chemical and enzymatic oxidation of phenolic compounds has been summarised in several books and reviews [1-4].

In view of the great biosynthetic importance and preparative utility of the formation of p-quinone, we have investigated the anodic oxidation of different 4-substituted α-naphthol derivatives. We wish to report the new electrochemical method for a synthesis of γ-lactone and δ-lactone (2),(3) [5].

Results and Discussion

The electrochemical synthesis described here provides a convenient preparative route to the corresponding heterocyclic products (2) and (3). Both electrochemical syntheses were carried out in an undivided cell at a Pt-anode and cathode under controlled potential. The anodic oxidation of α-naphthol derivatives (1a) and (1b) in neutral electrolyte system by potential from 0.8 - 1.7 V (vs Ag/0.01 N Ag^+) lead to the formation of the naphthoxenium-ion (D).

When the side chain of the α-naphthol derivative contain a nucleophilic group, then the ring closure product take place with the formation of the γ-lactone (2) and δ-lactone (3) derivatives.

For the purpose of the formation of addition product (6) at the electrochemically formed naphthoxenium cation (D), we repeated the same experiment but added water to the reaction mixture to obtain the water addition product (2´) and (3´).

The isolation of such products (2´) and (3´) was not possible because the tendency to form intramolecular addition product (2) and (3) was greater than the tendency of the formation of intermolecular nucleophilic addition product (2´) and (3´). In fact the later products are considered as γ and δ-lactone derivatives (2) and (3).

To investigate the effect of the substituent in the o-position with the
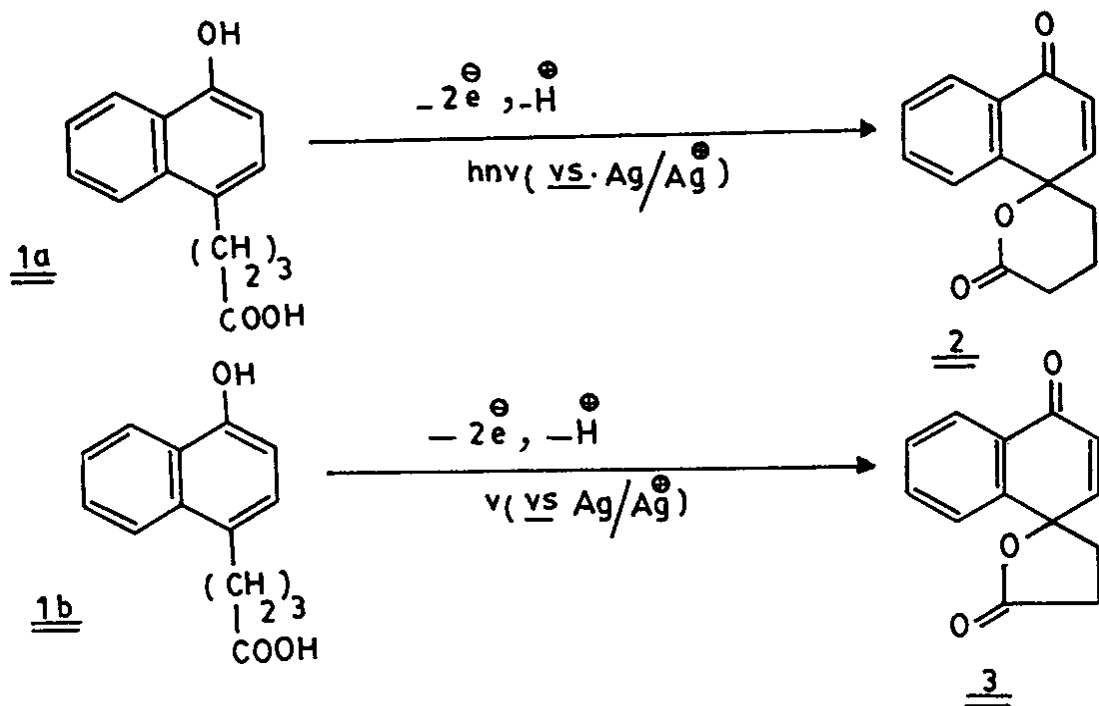
reaction product and yield, we have oxidised γ-(3-bromo-4-hydroxy-1-naphthyl)butyric acid (1c) under the same conditions of electrolysis. We obtain also the -lactone derivative (4) in 35% yield.

The high yield of product (4) was due to the presence of Br in o-position. The function of the Br in the o-position was to block the reaction tendency at the o-position (7) and this prevents the dimerisation of the oxidation products. The higher yield

was due to the high stability of the intermediate cation which permits the formation of the naphthoquinone structure.

The electrochemical oxidation of 4-hydroxy naphthyl acetic acid (1d) led to the formation of different products. As a main product, 4-hydroxy naphthaldehyde (8) was identified by the comparison of the R_f value.

The anodic oxidation of (4c) led to the formation of the quinomethide
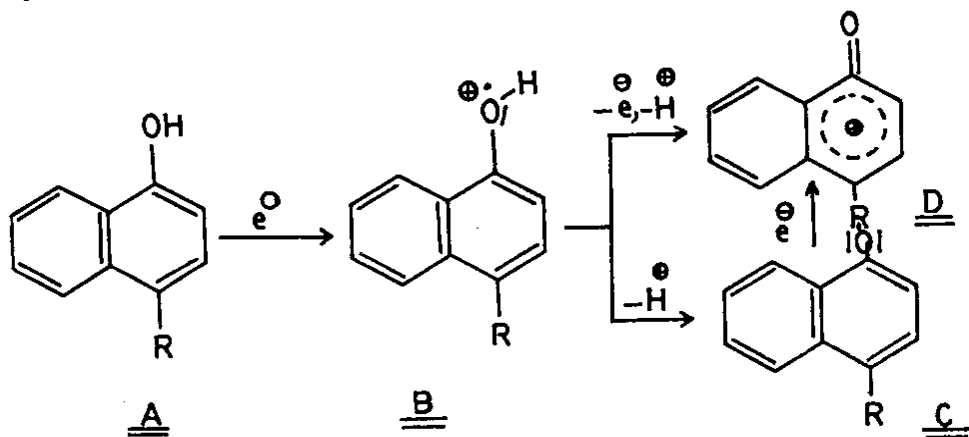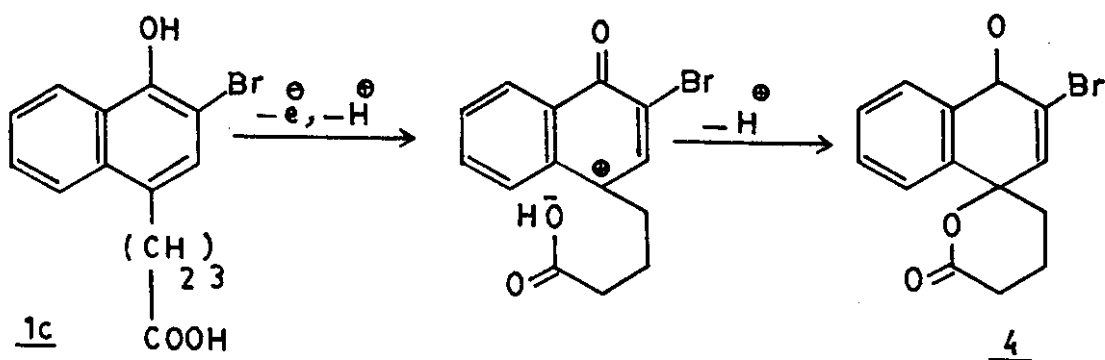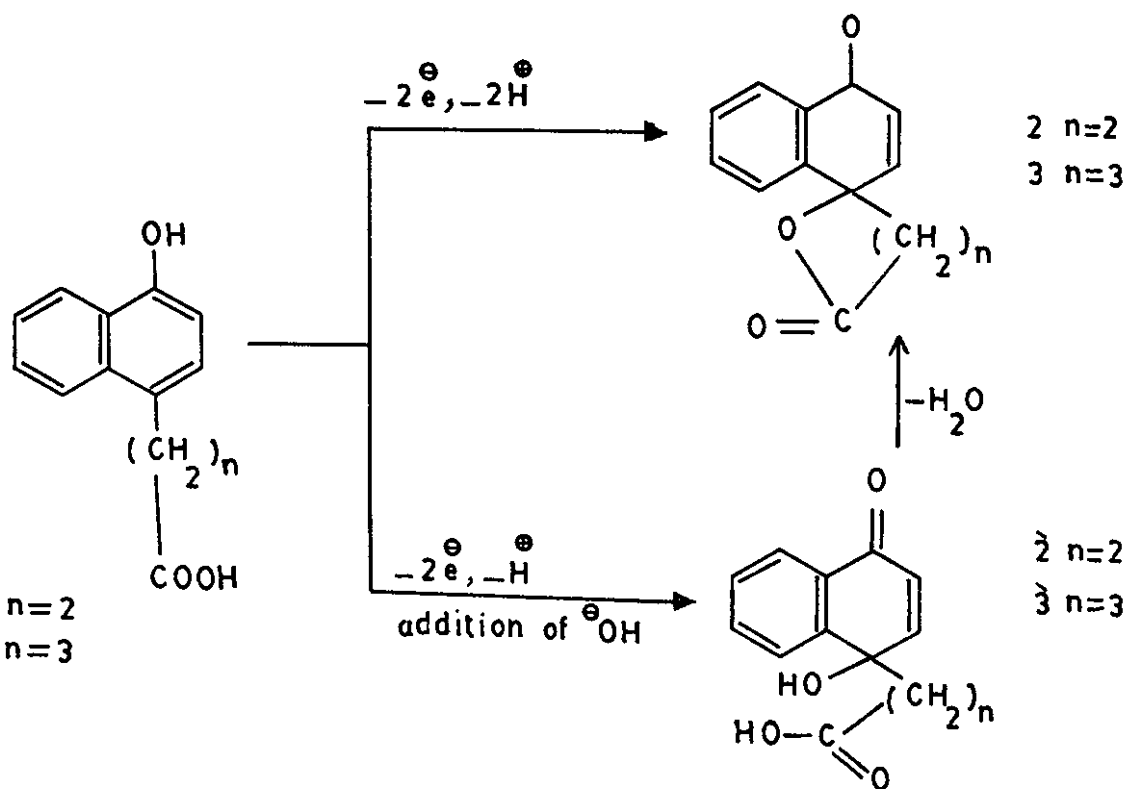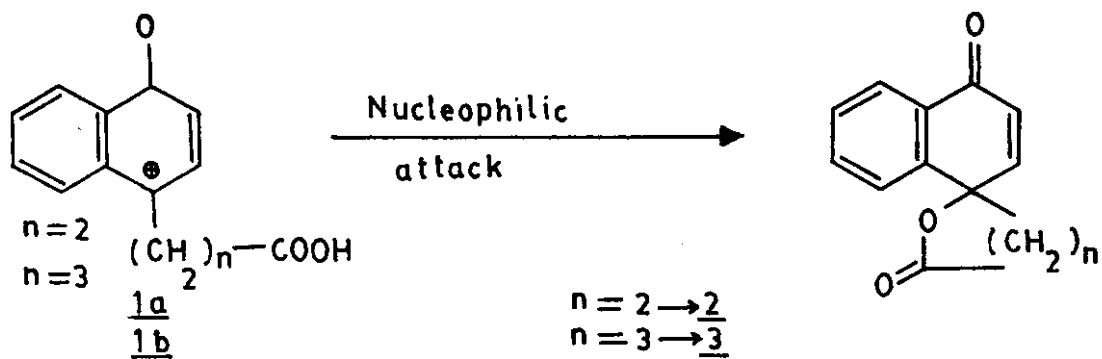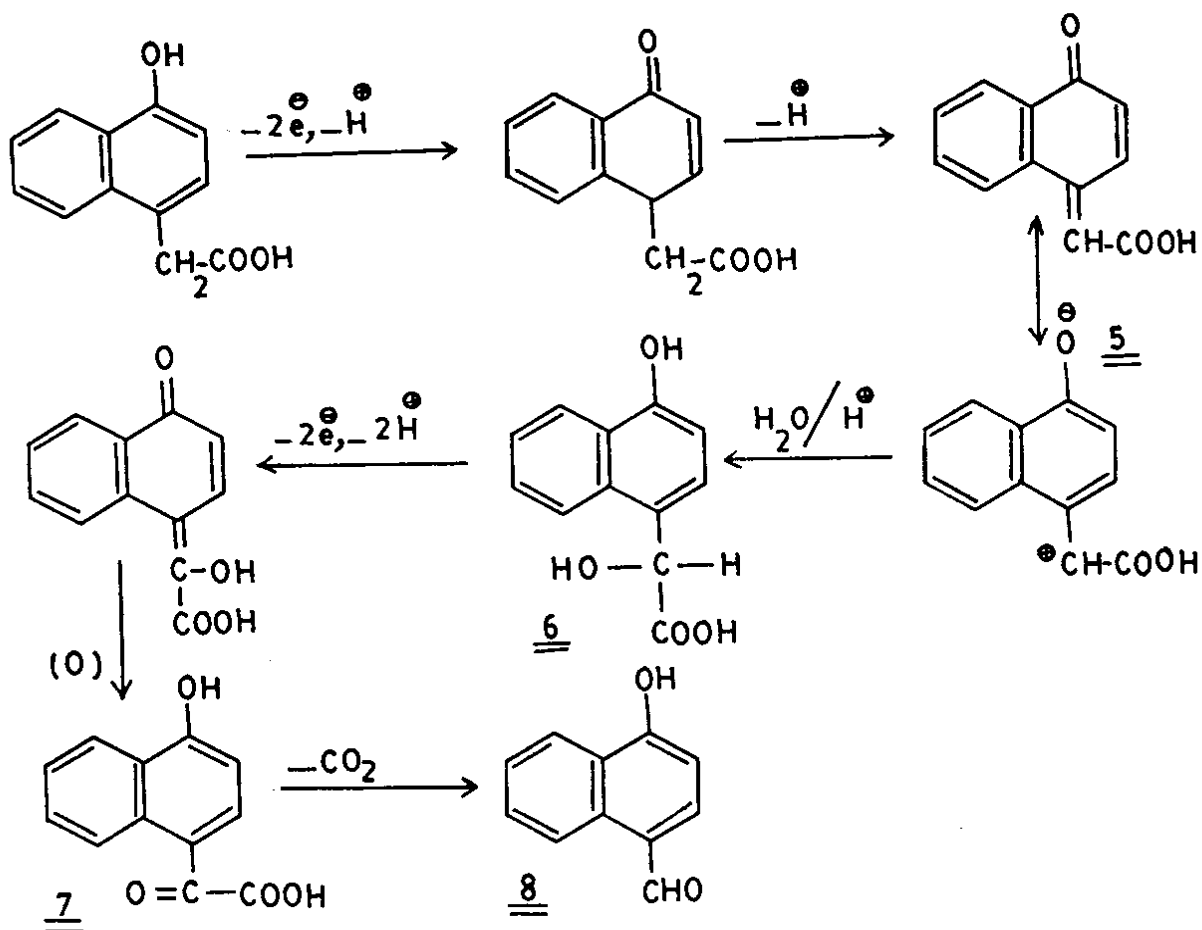
(5) which is thermodynmically stabi-lised by conjugation. The addition of water to quinomethide takes place to form the adduct (6) which is further oxidised to the α-keto acid (7). The latter is unstable and loses CO_2 to form the p-hydroxy naphthal-dehyde (8).

The electrochemical oxidation of 4-hydroxyacetonaphthone (1e) in pure acetonitrile and lithium perchlo-rate as a supporting electrolyte leads to the formation of naphtho-oxazole (9).

The attack of the solvent acetoni-trile to the orthro position of the formed naphthoxenium ion was obser-ved in other cases (8,9). In this

reaction, a five membered heterocyclic ring was formed in a one step re-action.

Experimental

Most of the anodic oxidations were performed by using two platinum anode and cathode. We also used the cell described by Rieker [6]. The reference electrode was Ag/10^{-2}N Ag$^+$ electrode. All reactions were rapidly stirred magnetically. For electrolysis at constant potential a potentiostat constructed from potential source, voltage scan generator VSG 72 and amplifier PCA 72C were used.

Electrolysis General

The α-naphthoi derivative to be oxidsed (2 g, 6-12 mmol) and lithium

Reaction scheme: **1e** → (CH₃CN/H₂O, $-2e$, $-H^{+}$) → **9**
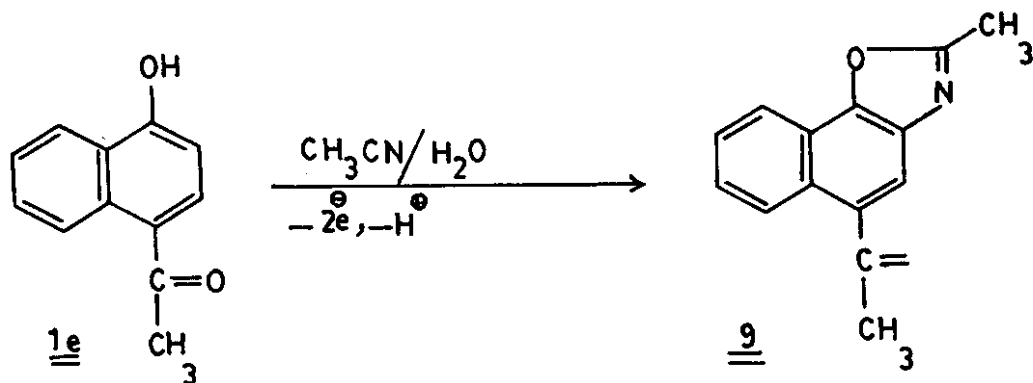
Naphthol Derivatives[a]	Oxidation Conditions	Products	M.P[b]	Yield
(1a) [10]	+1600 mV, Pt anode, 3h	(2)	156°C	23%
(1b) [11]	+1470 mV, Pt anode, 3.5h	(3)	122°C	25%
(1c) [12]	+1700 mV, Pt anode, 3h	(4)	142°C	35%
(1d) [13,14]	+1240 mV, Pt anode, 3h	(8)	-	-
(1e) [15]	1300 mV, Pt anode, 3.5h	(9)	171°C	32%

Product	IR(KBr) ν max cm^{-1}	NMR[c] δ ppm	Analysis C	H
(2)($C_{14}H_{12}O_3$)	1660,1620,1720	1.8-2.3(m,4H) 2.6(m,2H) 6.3,6.45,7.65,7.8 (m,2H) 7-8(m,4H)	R 73.6 F 73.5	5.2 5.1
(3) ($C_{13}H_{10}O_3$)	1660,1620,1720	2.6-3.1(m,4H) 6.5,6.6,7.45,7.55 (m,2H) 7.5-8.2(m,4H)	R 72.8 F 72.7	4.6 4.4
(4) ($C_{14}H_{11}BrO_3$)	1665,1620,1720	1.9-2.5(m,4H) 2.9-3.1 (m,2H) 7.5-8.3(m,5H)	R 54.7 F 54.6	3.5 3.5
(9) ($C_{14}H_{11}NO_2$)	1770,1680		R 74.6 F 74.6	4.8 4.9

(a) Samples prepared as described in these references.
(b) Melting point are uncorrected.
(c) DMSO is used as a solvent.

perchlorate as supporting electrolyte (1.86 g) were dissolved in 175 ml acetonitrile contained in the electrolysis cell. The electrolysis were carried out at constant potential (see table). After the oxidation time, the acetonitrile was evaporated to about 60 cc using the rotary evaporator, extracted with ether, washed with water and dried over sodium sulphate anhydrous. The oil produced after evaporation of ether was crystallized from suitable solvent and detected as usual.

The table shows the conditions of electrolysis of each substance, melting point, yield, IR, NMR and analysis of each product of electrolysis.

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