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Electro-oxidation of certain naphthalene derivatives

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Abstract Naphthalene and alkylnaphthalenes are electro-oxidized to give many products, of which 1,4-naphthoquinones and binaphthyls are the most stable, especially in the case of substrates, which are not substituted in α-positions. On the other hand, α-substituted naphthalenes give the respective naphthoquinols as the main products. Interestingly, 1,2-naphthoquinones are not separated as products, instead, a fragmentation of one of the rings leads to oxidation products, in which the 1,2-bond in naphthalene is broken to form dialdehydes or diketones. An anodic formation of binaphthyls is described, starting from alkyl-substituted naphthalenes, dissolved in acetone-water (1:1 v/v) and using $0.1\,M$ $(CH_3)_4N(BF_4)$ supporting electrolyte. Several isomeric binaphthyls were obtained depending on the substrates. The structure of the binaphthyls formed is discussed based on molecular orbital calculations using the AM1 program. Cyclic voltammetric oxidation curves are shown for naphthalene and three methyl derivatives.

Keywords Alkylnaphthalenes; Cyclic voltammetry; Electro-oxidation; Binaphthyls; AM1 method.

Introduction

Electro-oxidation is a unique technique of synthesis, because it does not require specific reagents. Other oxidation techniques employ reagents, *e.g.*, salts of metallic ions of higher positive charge, like Co^{3+}, Mn^{3+}, and Fe^{3+} or oxyanions, like $Cr_2O_7{}^{2-}$ or $MnO_4{}^{1-}$, which, however, introduce toxic metallic components into the reaction medium. There is, nevertheless, a limitation to electro-oxidations, because the mechanism is usually less clear, when an oxidation takes place at the electrode. The common mechanism of electrochemical oxidation states a radical cation formation:

$$AH_2 - e^- = (AH_2)^{+\bullet} \qquad (1)$$

where the species, starting on the left side, are an aromatic hydrocarbon and its radical cation – the mechanism dates back to the 1950s [1a–c]. The radical cations are reactive, and their secondary reactions determine the course of electrochemical oxidations. One of the typical regular reactions of radical cations is a reaction with water, which leads to hydroxylation of an aromatic system [2].

Thus, in course of anodic oxidations, ionic or molecular components of the medium, including a solvent and a supporting electrolyte may react with radical cations, as nucleophilic reagents. Also of importance may be adsorption and catalytic characteristics of the electrode promoting at times polymerization reactions. Naphthalene derivatives were chosen as model substrates, because they are readily available.

The purpose of this research was to make a survey of the reactivity of naphthalene derivatives, when subjected to an anodic oxidation [1c, 2]. For com-

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parison, the photochemical oxidation of naphthalene by dioxygen in presence of metallic salt catalysts evoked interest of many researchers. Among the formed products are: 1- and 2-naphthols, salicylic acid, 1,4-naphthoquinone, phthalic acid, and 2-formylcinnamaldehyde [3–10]. On the other hand, naphthols electro-oxidized gave maleic and phthalic acids [11, 12]. Alkylnaphthalenes have been oxidized preparatively using cerium ammonium nitrate to form aromatic aldehydes [13]. Electro-oxidation of alkylnaphthalenes was tried, however, these reactions suffered from low yields due to low selectivity and tar formation [14]. There were also indications that alkyl groups might migrate during the electro-oxidation, in agreement with earlier observations of a 1,2-shift of a substituent in electro-oxidations having radical cations, as unstable primary products [15]. In general, it has been observed that 2-alkylnaphthalenes produced foreseen products, like alkyl-substituted 1,4-naphthoquinones and 1,1′-binaphthyls, but 1-alkylnaphthalenes gave a variety of products due to the oxidation of both alkyl groups and of the aromatic ring [14, 15]. Most frequently, alkyl-substituted naphthoquinols were the major products of the electro-oxidation of 1-alkylnaphthalenes, similarly as was found in chemical oxidations [16, 17].

It seems that the alkyl groups in 1-alkylnaphthalenes block thermodynamically the most favorable oxidation course leading to 1,4-naphthoquinones. Instead, the oxidations may lead to the reaction of the alkyl group itself, formation of the alkyl-substituted naphthoquinols, and 1,2-shift of the alkyl substituent. The present paper supplies an additional experimental evidence about the course of electro-oxidations of several alkylnaphthalenes.

Results and discussion

It is hoped that electro-oxidations may produce some products, which are not otherwise obtainable easily. Electro-oxidations can be easily ascertained employing cyclic voltammetric technique (Fig. 1). As mentioned earlier, the species produced at the electrode are radical cations, formed according to Eq. (1). Radical cations become hydrated, and transform into the activated complex for follow-up reactions. As the positive electric charge and unpaired spin density are diffused over the whole aromatic molecular structure, various secondary reactions are possible. One of the most important reactions is an abstraction of a hydronium ion to form a neutral radical:

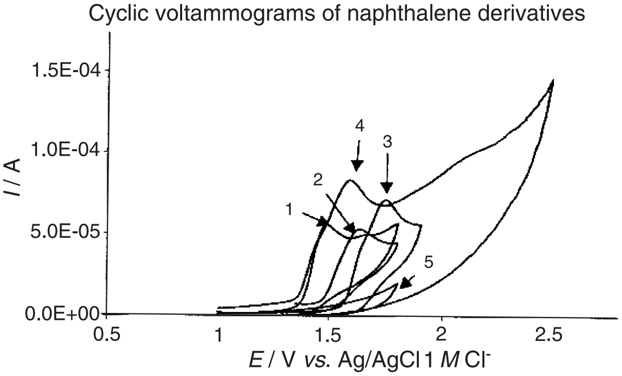

Fig. 1 Cyclic voltammetric curves of: *1* – 1,2-dimethylnaphthalene, *2* – 2-methylnaphthalene, *3* – 2,3-dimethylnaphthalene, *4* – 2,6-dimethylnaphthalene, and *5* supporting electrolyte alone. Measurement conditions as described in the Experimental section

$$(AH_2)^{+\bullet} + H_2O = (AH)^{\bullet} + H_3O^{+} \tag{2}$$

The radical on the right of Eq. (2) may react as follows: it can be re-oxidized (Eq. (3)) at the electrode or in solution by a radical cation, or it can dimerize (Eq. (4)):

$$(AH)^{\bullet} - e^{-} = (AH)^{+} \tag{3}$$

$$2(AH)^{\bullet} = HA - AH \tag{4}$$

The carbocation on the right of Eq. (3) can react with a nucleophile, *e.g.*:

$$(AH)^{+} + 2H_2O = (AH)OH + H_3O^{+} \tag{5}$$

The product may be hydroxylated in the ring or alkyl group, can again become re-oxidized by passing similar reaction stages, as shown by Eqs. (1) to (5). There is an important difference, however: compounds hydroxylated in aromatic rings are more easily oxidized, than their substrates. Thus, they cannot be isolated, but sometimes may be seen in trace amounts, like, *e.g.*, 1-naphthol in the case of the oxidation of naphthalene [14]. The final products, stable to further oxidation, are usually carbonyl compounds and, if alkyl substituents are not present in α-positions – quinones. Usually, the ring containing alkyl substituents is more reactive, than one without them, thus, 2-methylnaphthalene is electro-oxidized to form 2-methyl-1,4-naphthoquinone, 6-methyl-1,4-naphthoquinone, and 4 isomeric binaphthyls in a ratio of approximately 10:3:1 according to comparison of GC signal intensities in GC-MS analysis [14].

In the case of α-methyl substituted naphthalenes, stable oxidation products are naphthoquinols, *e.g.*, in the case of electro-oxidation of 1-methylnaphthalene, the main product is 4-methylnaphthoquinol or 4-methyl-4-hydroxynaphthalen-1(4*H*)-one, which has been synthesized earlier [17]. Other courses of the electro-oxidation are also possible:

1. oxidation of the methyl group to 1-naphthylcarbinol, and further to 1-naphthaldehyde;
2. complete oxidation of the methyl group with formation of 1,4-naphthoquinone; and
3. 1,2-shift of the methyl group with formation of 2-methyl-1,4-naphthoquinone (vitamin K_3), which seems to be the most stable oxidation product.

The cases 2 and 3 have been observed during the anodic oxidation of certain α-substituted naphthalenes [18].

Binaphthyls form in anodic oxidations of β-methyl substituted naphthalenes. Thus, the electro-oxidation of 2-methylnaphthalene is accompanied, among other products, by four GC-MS peaks having $m/e = 282$, characteristic for dimethyl-binaphthyls, of steeply declining intensity in the direction of longer retention times. The actual structures of the four dimethylbinaphthyls have not been determined, however, it seems rational that naphthyl radicals are linked by the more reactive 1 and 1′ positions. *A priori*, ten isomers of 2,2′-dimethyl-1,1′-binaphthyls are possible, four of which have a plane of symmetry (Fig. 2). It is interesting to consider, which four isomers are actually synthesized. The intensity ratios of the four isomers detected by GC-MS are about 20:10:1.5:1, decreasing toward longer retention times – the GC relative retention times of the four isomers are: 1.000:1.017:1.034:1.048. The first two isomers are much more abundant, than the other two. It is simpler to describe the binaphthyls formed during electro-oxidation of symmetrical dimethylnaphthalenes, *i.e.* 2,6-dimethylnaphthalenes and 2,3-dimethylnaphthalenes. Here two isomers are formed for each of the two substrates, and their GC peak intensities are comparable for a pair, while theoretically three $\beta,\beta',\beta'',\beta'''$-tetramethyl-1,1′-binaphthyl isomers are possible each for the two symmetrical dimethylnaphthalenes, as substrates (Fig. 3).

In the case of electro-oxidation of 1,2-dimethylnaphthalene only a trace of tetramethylbinaphthyl is observed, as a relatively very small peak of $m/e = 310$ in GC-MS analysis. There is, however, an isolated product of the determined composition $C_{21}H_{18}O_2$, whose structure is proposed to be that of 3′,4′-dimethyl-1′-naphthyl 3-acetoxyphenyl ketone. This new product is formed due to a partial oxidation of one of the rings, having methyl substituents, in an originally produced 3,3′,4,4′-tetramethyl-1,1′-

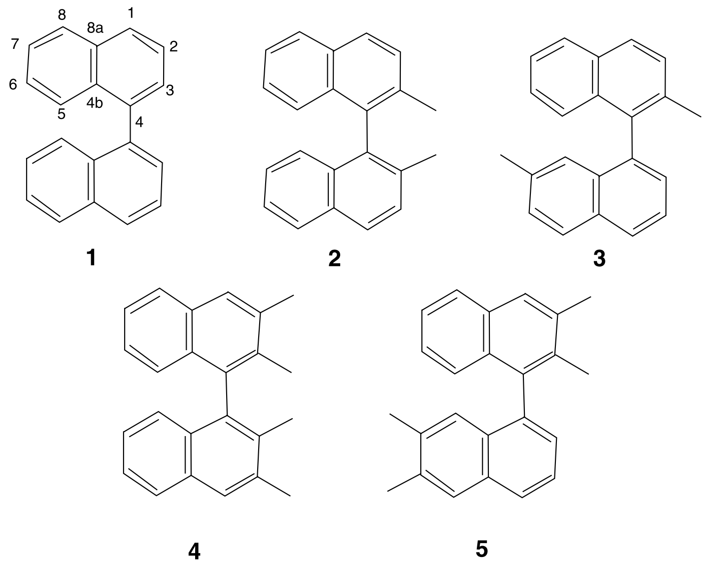

Fig. 2 The planar structures of the isolated binaphthyls: **1** – 1,1′-binaphthyl, **2** – 2,2′-dimethyl-1,1′-binaphthyl, **3** – 2,7′-dimethyl-1,1′-binaphthyl, **4** – 2,2′,3,3′-tetramethyl-1,1′-binaphthyl, and **5** – 2,3,6′,7′-tetramethyl-1,1′-binaphthyl

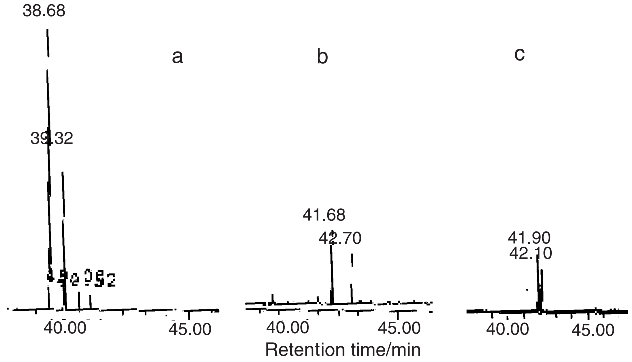

Fig. 3 (a) The 4 GC-MS lines of $m/e = 282$ of dimethyl-1,1′-binaphthyls formed on electro-oxidation of 2-methylnaphthalene and (b) 2 GC-MS lines of $m/e = 310$ of tetramethyl-1,1′-binaphthyls obtained on electro-oxidation of 2,3-dimethylnaphthalene; and (c) 2 GC-MS lines of $m/e = 310$ of tetramethyl-1,1′-binaphthyl obtained on electro-oxidation of 2,6-dimethylnaphthalene. The scales are arbitrary and not exactly the same

binaphthyl, which has been observed in trace amounts by GC-MS. The remaining product of the oxidation of a ring is pyruvaldehyde, which is water soluble, and cannot be extracted with chloroform for a later GC-MS detection. The major product of electro-oxidation of 1,2-dimethylnaphthalene is, however, 3,4-dimethyl-4-hydroxynaphthalen-1(4*H*)-one (3,4-dimethylnaphthoquinol), by analogy with similar reactions of 1-methylnaphthalene and 1-ethylnaphthalene, as substrates of electro-oxidation (Fig. 4).

The product of electro-oxidation of 1,2-dimethylnaphthalene described above of $m/e = 302$ forms in a similar way, like a small yield of 2-formylcinamaldehyde is obtained due to an oxidative opening of a ring. The same product was observed from naphthalene during photochemical in air oxidation or ozonolysis by microwave discharge of oxygen; this compound can exist as two diastereomers of which the (*E*)-isomer is the more stable one [3–9].

Binaphthyl derivatives

It is well known that dehydrodimeric products are formed during the oxidation of aromatic hydrocarbons or their derivatives [19]. Similar reactions are called *Scholl* reactions, and are conducted with oxidants, strong acids as catalysts, and at high temperatures. Usually, however, yields are low, because of the harsh reaction conditions [20]. Electrochemical, anodic oxidations can also lead to dehydrodimeric products [14, 19d, 21]. Usually, such products are accompanied by other oxidation products, like quinones, quinols, or products having alkyl groups oxidized. The separation and characterization of binaphthyls is difficult because of similarity of structures and close chromatographic retention times. They are, however, interesting compounds, and their structure may better be rationalized by using molecular orbital calculation programs like AM1 [22].

The results of the present calculations are shown in Table 1 and the structures of some of the compounds are given in Fig. 2. All the alkyl-1,1′-binaphthyls studied have a similar energy of the highest occupied molecular orbital, E_{HOMO}, and the calculated heats of formation, *HOF*, are similar for a group of isomers.

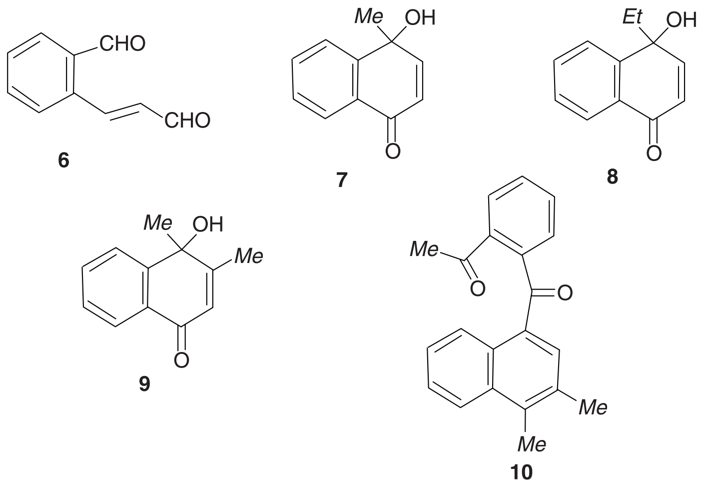

Fig. 4 Products obtained by electro-oxidations of: (a) naphthalene, **6**; (b) 1-methylnaphthalene, **7**; (c) 1-ethylnaphthalene, **8**; (d) 1,2-dimethylnaphthalene, **9** and **10**. Numbers correspond to isolated compounds described in the Experimental section

Table 1 Calculated energy of HOMO molecular orbital, calculated Heat of Formation (*HOF*), and calculated structural characteristics such as: the angle between binaphthyl planes, dipole moment and an approximate volume of molecule, for chosen binaphthyl compounds, calculated according to the AM1 program [22]

No.	Compound	E_{HOMO}/eV	*HOF*/ kJ mol^{-1}	Angle between binaphthyl planes/°	Dipole moment/D	Approximate volume of molecule/Å^3
1	1,1′-binaphthyl (**1**)	−8.49	368.9	69.22	0.051	464
2	2,2′-dimethyl-1,1′-binaphthyl (**2**)	−8.54	317.5	87.07	0.350	458
3	3,3′-dimethyl-1,1′-binaphthyl	−8.43	329.8	69.90	0.320	522
4	2,3′-dimethyl-1,1′-binaphthyl	−8.51	311.9	82.80	0.412	412
5	2,6′-dimethyl-1,1′-binaphthyl	−8.51	310.9	82.75	0.483	392
6	2,7′-dimethyl-1,1′-binaphthyl (**3**)	−8.51	311.7	82.92	0.416	655
7	2,2′,3,3′-tetramethyl-1,1′-binaphthyl (**4**)	−8.48	266.6	86.43	0.715	574
8	2,3,6′,7′-tetramethyl-1,1′-binaphthyl (**5**)	−8.50	254.3	88.98	0.833	485
9	6,6′,7,7′-tetramethyl-1,1′-binaphthyl	−8.33	251.2	68.87	0.701	755
10	2,2′,6,6′-tetramethyl-1,1′-binaphthyl	−8.46	252.8	87.13	0.069	870
11	3,3′,6,6′-tetramethyl-1,1′-binaphthyl	−8.34	241.7	70.27	0.017	733
12	2,3′,6,7′-tetramethyl-1,1′-binaphthyl	−8.42	247.3	82.82	0.055	502

The planes of the two naphthyl rings form a dihedral angle, which can be calculated using the following formulas of solid analytical geometry: two planes P_1 and P_2 are represented by a general equation:

$$A_n x + B_n y + C_n z + D_n = 0 \qquad (6)$$

where $n = 1$ for plane P_1 and $n = 2$ for plane P_2, and by their normal vectors $\mathbf{N}_1\{A_1, B_1, C_1\}$ and $\mathbf{N}_2\{A_2, B_2, C_2\}$. The dihedral angle φ between the two planes follows from the scalar product of their normal vectors:

$$\mathbf{N}_1 \cdot \mathbf{N}_2 = \mathbf{N}_1\ \mathbf{N}_2 \cos\varphi \qquad (7)$$

where $0 \leq \varphi \leq \pi$ and the bracketed terms are moduli of the normal vectors. The respective vector components $\{A_1, B_1, C_1\}$ and $\{A_2, B_2, C_2\}$ for the two planes, representing both naphthyl radicals, may be calculated from coordinates of three points each lying on the planes, *e.g.*, coordinates of 3 carbon atoms each in the two rings directly linked by the single bond; the appropriate mathematical formula is given in a mathematical handbook [23].

As is seen in Table 1, the angle between naphthyl planes changes from values of 68–70° for binaphthyl, 3,3′-dimethyl-1,1′-binaphthyl, 3,3′,6,6′- and 6,6′,7,7′-tetramethyl-1,1′-binaphthyls, 82° for 2,3′-, 2,6′-, and 2,7′-dimethyl-1,1′-binaphthyls and 2,3′,6,7′-tetramethyl-1,1′-binaphthyl, to 86–88° for 2,2′-dimethyl-1,1′-binaphthyl, 2,3,2′,3′-, 2,3,6′,7′-, and 2,2′,6,6′-tetramethyl-1,1′-binaphthyls. For all the compounds studied, the two naphthyl rings are out of plane, and in the case of the last group of compounds are almost perpendicular one to another. How accurate the calculated values are in relation to measured ones has yet to be seen, because no crystallographic data for the compounds were found in literature yet. It is interesting to try to explain what number of isomers of the studied compounds are possible theoretically, and how many are observed in reality. Judging on the values of the electron density of carbon atoms in alkylnaphthalenes and their radical cations, coupling of naphthyls by a nucleophilic/electrophilic mechanism takes place practically exclusively at 1,1′ carbon atoms, because the radical cations have the highest positive charges at these positions.

The structure of some of the isomers was resolved using 400 MHz NMR. The two most abundant isomers **2** and **3** present according to GC-MS line intensities in the ratio of 1.7 to 1.0, show following lines in the alkyl hydrogen region: strong line at 2.03 ppm (rel. intensity: 16.7) and two weaker lines at 2.11 ppm (rel. intensity: 6.1) and 2.27 ppm (rel. intensity: 5.0). It follows that the strong line at 2.03 ppm belongs to the 2,2′-dimethyl-1,1′-binaphthyl, while the weaker lines belong to the 2,7′-dimethyl-1,1′-binaphthyl isomer.[1] The resolution of the second isomer follows from the comparison

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[1] The H NMR (400 MHz, $CDCl_3$) for the 2,2′-dimethyl-1,1′-binaphthyl was resolved as follows: $\delta = 2.03$ (s, 2-*Me*, 2′-*Me*), 7.04 (dd, $J = 8.4$, 1.0 Hz, H8/H8′), 7.20 (ddd, $J = 8.4$, 6.8, 1.2 Hz, H7/H7′), 7.39 (ddd, $J = 8.2$, 6.8, 1.2 Hz, H6/H6′), 7.50 (d, $J = 8.5$ Hz, H3/H3′), 7.88 (bt, $J = 8.3$ Hz, H4/H4′, H5,H5′) ppm. The lines for the 2,7′-dimethyl-1,1′-binaphthyl isomer could not be seen distinctly for a complete resolution of its NMR spectrum, too.

of the positions of the alkyl-H NMR lines at 2.11 and 2.27 ppm with those measured for 2,2′,4,4′-, 3,3′,4,4′-, and 4,4′,6,6′-tetramethyl-1,1′-binaphthyls [19d–e]. In the case of the first isomer above the assignment of the lines to positions was supported using nuclear *Overhauser* experiment [19e]. It follows that the NMR line for methyl-H at carbon-2 is the smallest and equal to $\delta = 1.99$ ppm, while those for methyl-H at carbon-3 and carbon-6 are both equal to $\delta = 2.54$ ppm (for methyl-H at carbon-4 is $\delta = 2.71$–2.78 ppm). Thus, the second most abundant isomer **3** in Fig. 2 has two unequivalent methyl groups, one of which is at carbon-2 (line at $\delta = 2.11$ ppm), while the other should be at carbon-7 (line at 2.27 ppm), because the latter's chemical shift value is appreciably smaller than that expected for methyl groups at carbons-3 and 6, as explained above.

The above assignments are, as well, supported by the resolution of the structures of the two tetramethyl-1,1′-binaphthyls **4** and **5**, obtained in the electro-oxidation of 2,3-dimethylnaphthalene as GC-MS lines of relative intensities 2.3 to 1.0 in the direction of longer retention times, and analyzed by NMR.[2] It follows that the two isomers may have the structures of 2,2′,3,3′-tetramethyl-1,1′-binaphthyl and 2,3,6′,7′-tetramethyl-1,1′-binaphthyl. The assignment of the structure of the second isomer is deduced by comparison with the corresponding NMR lines of other isomers of alkylated binaphthyls, as shown above.[3]

The assignment of structures to the four isomers of alkyl derivatives of dimethyl-1,1′-binaphthyl may agree with the direction of change of residence times in GC, assuming that the retention time increases with increasing dipole moments of a molecule. As is shown in Table 1, 2,7′-dimethyl-1,1′-binaphthyl has a calculated dipole moment of 0.416 debye, which is higher than the calculated dipole moment of the 2,2′-dimethyl-1,1′-binaphthyl isomer, *i.e.* 0.350 D. Thus, the first isomer is expected to have a longer retention time, which is actually confirmed experimentally (Fig. 3a). Similarly, 2,3,6′7′-tetramethyl-1,1′-binaphthyl has a calculated dipole moment of 0.833 D, which is also higher than that for isomeric 2,2′,3,3′-tetramethyl-1,1′-binaphthyl (0.715 D). Consequently, the former isomer should have a longer retention time in gas chromatography than the latter one, which is actually confirmed experimentally (Fig. 3b).

It is interesting to try to explain, why certain alkylated binaphthyl isomers form, and others do not. The answer may lie in the structure of the activated complex. According to *Eberson et al.* [19d], there are several possible routes leading to dehydrodimers, starting from the radical cations of the substrate aromatic hydrocarbon ($Ar\mathrm{H}_2$), *e.g.*:

$$Ar\mathrm{H}_2 - \mathrm{e}^- = (Ar\mathrm{H}_2)^{+\bullet} \tag{8}$$

$$2(Ar\mathrm{H}_2)^{+\bullet} = Ar(\mathrm{H}_2) - Ar(\mathrm{H}_2)^{2+} \tag{9}$$

and

$$(Ar\mathrm{H}_2) - (Ar\mathrm{H}_2)^{2+} - 2\mathrm{H}^+ = (Ar\mathrm{H}) - (Ar\mathrm{H}) \tag{10}$$

Table 2 Net charges at C-atoms and unpaired spin densities in the singly occupied molecular orbital SOMO of radical cations calculated according to the AM1 program [22]

Radical cation of, C-atom positions in the nucleus	Net charges at C-atoms	Unpaired spin densities at C-atoms
Naphthalene:		
1, 4, 5, 8	0.029	0.184
2, 3, 6, 7	−0.090	0.066
4b, 8a	−0.104	0.000
2-Methylnaphthalene		
1	0.010	0.198
2	0.022	0.105
3	−0.139	0.029
4	0.035	0.167
5	0.003	0.156
6	−0.060	0.095
7	−0.118	0.036
8	0.030	0.183
9	−0.095	0.004
10	−0.100	0.006
Methyl-C	−0.220	0.006

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[2] The mixture of the two isomers gave two sets of higher field methyl-H lines, having relative intensities of 4:1, the more intensive set of two lines at $\delta = 1.94$ and 2.54 ppm, and the less intensive set of four lines at $\delta = 2.01$, 2.18, 2.41, and 2.54 ppm. The fully resolved NMR (400 MHz, CDCl_3) spectrum for 2,2′,3′3′-tetramethyl-1,1′-binaphthyl is the following: $\delta = 1.94$ (s, 2-*Me*, 2′-*Me*), 2.54 (s, 3-*Me*, 3′-*Me*), 6.95 (dd, $J = 8.4$, 1.0 Hz, H8/H8′), 7.12 (ddd, $J = 8.4$, 6.8, 1.2 Hz, H7/H7′), 7.35 (ddd, $J = 8.2$ Hz, 6.8, 1.2 Hz, H6/H6′), 7.74 (s, H4/H4′), 7.81 (d, $J = 8.2$, H5/H5′) ppm.

[3] The NMR (400 MHz, CDCl_3) lines assignment for methyl-H in 2,3,6′,7′-tetramethyl-1,1′-binaphthyl: $\delta = 2.01$ (s, 2-*Me*), 2.18 (s, 7′-*Me*), 2.41 (s, 6′-*Me*), 2.54 (s, 3-*Me*) ppm. The NMR lines for this isomer in the aromatic region could not be singled out well enough to be resolved.

It is postulated that the bond will form where there is a high unpaired spin density in the respective radical cations, *i.e.*, in 1, 4, 7, and 10 (all α) positions of the naphthalene nucleus, as the two unpaired electrons may form a σ-bond, *vide* Table 2. It is also possible that orbital symmetry plays a role in the formation of σ-bond, and this condition limits the number of isomers of binaphthyl compounds, which are produced by the postulated mechanism above [24].

Experimental

In the course of electro-oxidation, lasting usually about 2 h, a charge of 2–7 electrons per molecule of substrate was transferred, while approx. 0.5–1 mmol of substrate was taken to reaction. The conditions of the galvanostatic electrolysis have been described earlier [14, 24]. Cyclic voltammetry was performed using Eco Cell (Holland) AutoLab PGST12 instrument, Metrohm cell, glassy carbon disk working electrode of dia. 3 mm, and $AgCl/Cl^-$ (1 *M* KCl) reference electrode at room temp. (*c.* 22°C). The naphthalene and derivatives were dissolved in acetone:water solution (1:1 *v/v*), containing 0.1 *M* $(CH_3)_4N(BF_4)$ supporting electrolyte. The potential rate was 0.02 V/s.

GC-MS analyses were performed using electron ionization (EI) with Hewlett-Packard GCMS system containing HP 5890 II gas chromatograph coupled directly to MSD 5972A mass-sensitive detector. NMR spectroscopy was performed using Varian 400 MHz instrument.

The following products were identified by GC-MS, NMR (400 MHz, $CDCl_3$), and HR-MS, and their structures are shown in Fig. 4: 2-formylcinammaldehyde (**6**) by GC-MS and ^1H NMR [6, 8, 9, 25]; 4-methyl-4-hydroxynaphthalen-1(*4H*)-one (4-methylnaphthoquinol) (**7**) by GC-MS [27]; 4-ethyl-4-hydroxynaphthalen-1(*4H*)-one (4-ethylnaphthoquinol) (**8**), MS *m/e* (% relative intensity) = 188 (10), 172 (5), 159 (100), 141 (3), 131 (20), 115 (8), 103 (19), 89 (2), 77 (31); 3,4-dimethyl-4-hydroxynaphthalen-1(*4H*)-one (3,4-dimethylnaphthoquinol) (**9**) by GC-MS and NMR [16]; 3′,4′-dimethyl-1′-naphthyl 3-acetoxyphenyl ketone (**10**), MS: *m/e* (% relative intensity) = 302 (81), 287 (56), 269 (7), 259 (20), 245 (10), 228 (4), 215 (19), 202 (6), 189 (2), 183 (100), 169 (6), 155 (26), 147 (37), 136 (22), 115 (16). ^1H NMR: $\delta = 8.91–8.89$ (m, 1H, C-8), 8.13–8.10 (m, 1H), 7.78–7.50 (m, 7H, arom.), 2.64 (s, 3H, CH_3–C-4), 2.48 (s, 3H, CH_3–CO), 2.39 (s, 3H, CH_3–C-3) ppm; HR-MS: found 302.13147, calcd 302.13068 for $C_{21}H_{18}O_2$.

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