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Electroorganic reactions. Part 56: Anodic oxidation of 2-methyl- and 2-benzylnaphthalenes: factors influencing competing pathways☆

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Abstract—A systematic investigation of the anodic oxidation in nucleophilic media of 2-methyl and 2-benzylnaphthalenes, substituted at the 6-position in the naphthalene nucleus and at the 4-phenyl position of the benzylic side chain, has been carried out to identify factors favouring side-chain substitution. Cyclic voltammetry confirms that 6-substitution has a profound effect on the oxidation potentials of the naphthalene nucleus and ^{13}C chemical shifts indicate polar effects at the benzylic carbon. However, little side-chain anodic oxidation is observed under any conditions tried; the radical–cations of electron-rich substrates preferentially dimerise and a strongly electron-withdrawing substituent at the 6-position ($EtOSO_2$) promotes nuclear substitution. In contrast, oxidation with DDQ in aqueous acetic acid gives efficient side-chain oxidation for electron rich substrates, consistent with hydride transfer, possibly intramolecularly via a charge transfer complex.

The anodic oxidation of alkylaromatics gives nuclear and side-chain substitution in nucleophilic solvents and dimerisation and other combination reactions in non-nucleophilic media.[1–3] Oxidation of toluene (**1a**) in acetic acid[4] gives predominantly *o*- and *p*-acetoxytoluene together with side-chain acetoxylation. In methanol side-chain substitution may result in the formation of the corresponding acetals as precursors to the aldehydes. Nuclear substitution in methanol often leads to further, *ipso*, substitution eventually to give quinone ketals.[5,6] In contrast, mesitylene is oxidised anodically in CH_2Cl_2–Bu_4NBF_4 (0.1 M) electrolyte to give a dimer.[1] The side-chain oxidation process is synthetically important and has been developed into at least one industrial process, a recent example[7] being the conversion of 4-*t*-butyltoluene into 4-*t*-butylbenzaldehyde as the anodic component of a 'paired electrosynthesis'.

The side-chain oxidation of toluene derivatives may be made quite selective. By analogy, derivatives of naphthalene-2-carboxaldehyde are likely to be good starting materials for the elaboration of functionality at the 2-position to give analogues of compounds with useful biological activity, including non-steroidal anti-inflammatory compounds. However, the conversion of 2-methylnaphthalenes, into naphthalene-2-carboxaldehydes is likely to be more problematic because of the greater opportunity for nuclear substitution in the electron-rich arene ring and of dimerisation, known to occur in electron-rich arenes.[1]

We report here a systematic exploration of the anodic oxidation of derivatives of 2-methylnaphthalene (**2**) with a view to identifying structural features or reaction conditions that influence the competition between nuclear substitution, dimerisation and side-chain oxidation. The pattern of substitution in the starting materials is designed to influence both the electron demand in the arene ring and the acidity of the 2-methylene protons. It is known that the benzylic hydrogens are very acidic in radical–cations (toluene has pK_a ca. 40, whereas the corresponding radical–cation has pK_a 11)[8] but the thermodynamic acidity may not be directly reflected in the kinetic acidity and deprotonation may still be outrun by competing nuclear substitution and by dimerisation. Systematic variation of substituents Y in compounds **2** should in principle considerably influence the electron demand and hence acidity of the 2-methylene protons in the radical–cations.

1. Results and discussion

1.1. Anodic oxidation of toluene derivatives

Optimum conditions were sought for the direct anodic side-chain oxidation of the 2-methylnaphthalenes by studying the analogous conversion of toluene derivatives. In the event no improvement was found on the conditions

☆ For part 55, see Ref. 40.

Keywords: electrochemical oxidation; alkylnaphthalenes; radical–cations.

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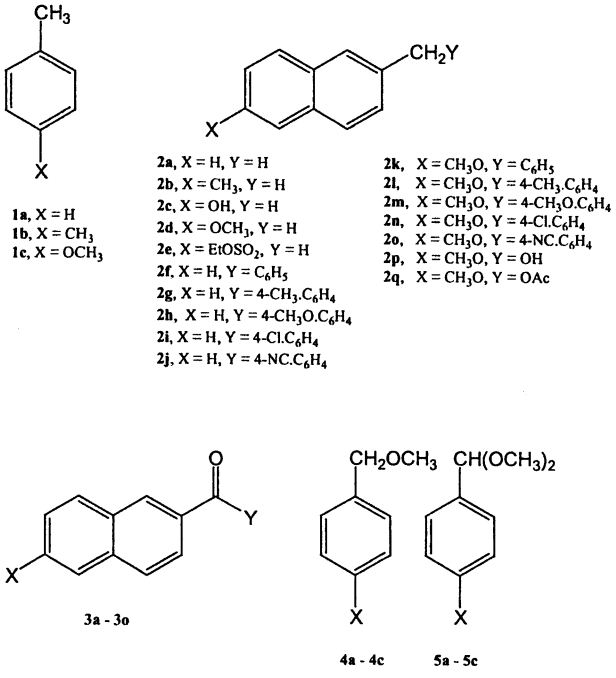
Table 1. Constant current electrolysis of toluene derivatives in methanol

Starting compound	E^0 (V vs. SCE)[a]	Products (%)
1a	2.35	Complex mixture[b]
1b	2.06	**5b** (72) **6b** (12) [**7b**+**8b**] (14)
1c	(1.68)[c]	**5c** (81) [**7c**=**8c**] (6)

Pt electrodes, undivided cell, MeOH–KF (0.15 M), 64 mA cm^{-2}, 4.2 F.
[a] CF_3CO_2H–$(CF_3CO)_2O$ (7% v/v)–Bu_4NClO_4 (0.1 M).
[b] ^1H NMR shows no evidence of side-chain substitution.
[c] $E_{1/2}$, CH_3CN–Et_4NClO_4 (0.1 M); Ref. 12.

established by the BASF group[9–11] although for convenience platinum anodes were used, rather than carbon, for the relatively small-scale reactions described here. The formulae of the starting materials (**1**) and products (**4**–**8**) are listed and the results of preliminary electrolyses are given in Table 1.

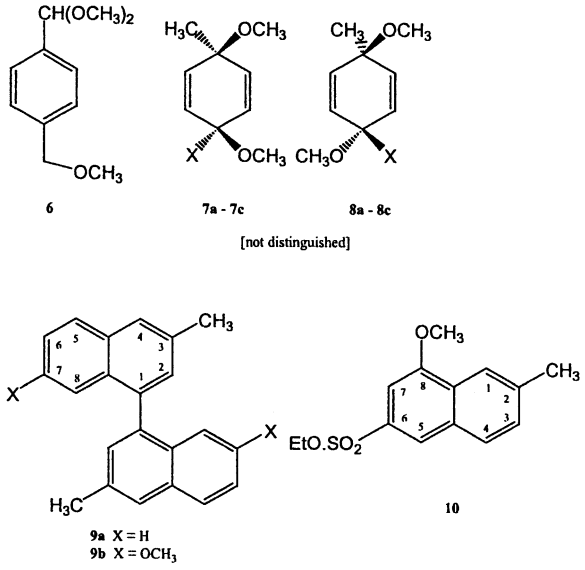


The BASF conditions are probably optimal for side-chain substitution but toluene is not amenable to useful conversion under these conditions. Electron donating substituents at the *para* position enhance side-chain substitution. From the ratios of [**5**+**6**]/[**7**+**8**] it is inferred that methoxyl (ratio 81/6=13.7) is more effective than methyl (ratio 84/14=6) in promoting side-chain substitution.

1.2. Anodic oxidation of naphthalene derivatives 2a, 2d, 2e

Essentially using the BASF conditions, the more successful preparative results for the anodic oxidation of the 2-methyl-6-substituted-naphthalenes are summarised in Table 2.

The reactions were not clean but according to ^1H NMR only a trace amount of side-chain substituted product was formed (from **2a**). It is clear that dimer formation (**9a** and **9b**) is preferred for the electron rich compounds, and that the 6-methoxyl substituent greatly enhances dimerisation. In contrast the strongly electron-withdrawing substituent $EtOSO_2$ suppresses dimerisation and encourages nuclear substitution, to give **10**. The characterisation of the products of these electrolyses is described in Section 2.



1.3. Oxidation potentials and ^{13}C NMR chemical shifts

In the toluene cases electron donation into the ring encourages side-chain substitution over nuclear substitution, whereas in the 2-methylnaphthalenes electron-withdrawal encourages nuclear substitution, which is

Table 2. Constant current electrolysis of 2-methylnaphthalene derivatives in methanol

6-Substituent (compound)	Concentration (M)	Solvent	Supporting electrolyte	Current density (mA cm^{-2})	F	Conversion[a] (%)	Side-chain[b] (%)	Dimers[c] (%)
H (**2a**)	0.60	MeOH	KF	64	4.3	>95	0	8 (**9a**)
H (**2a**)	0.55	MeOH	KF	48	5.3	>95	ca. 5	23 (**9a**)
H (**2a**)	0.14	MeOH/CH_2Cl_2	H_2SO_4	10	1.8	>95	0	8 (**9a**)
MeO (**2d**)	0.09	MeOH	KF	16	4.8	>90	8	9 (**9b**)
MeO (**2d**)	0.13	MeOH/CH_2Cl_2	H_2SO_4	10	2.2	89	0	72 (**9b**)
EtO·SO_2 (**2e**)	0.06	MeOH	KF	16	4.0	90	0	0
EtO·SO_2 (**2e**)	0.06	MeOH/CH_2Cl_2	H_2SO_4	20	2.0	36[d]	0	0

Pt electrodes, undivided cell.
[a] Based on recovered starting material; the balance of products were intractable tars.
[b] By ^1H NMR inspection of the crude product.
[c] See Section 2 for assignment of structure.
[d] Crude product appeared to be, by ^1H NMR, a mixture of nuclear mono-methoxylated products from which **10** was isolated in 27% yield.

Table 3. Oxidation potentials and chemical shifts for 2- and 6- substituted naphthalenes

Compound	6-Substituent	2-Substituent	E_p[a]/SCE	δ (^{13}C)	δ (^{1}H)
2a	H	CH_3	1.75	21.64[b]	–
2b	CH_3	CH_3	1.70	21.57[b]	–
2c	OH	CH_3	1.43	21.93	2.47
2d	OCH_3	CH_3	1.41	21.54	2.45
2e	$EtOSO_2$	CH_3	2.17	21.98	2.53
2f	H	C_6H_5	1.82	42.14	4.13
2g	H	4-CH_3·$C_6H_4CH_2$	1.83	41.80	4.09
2h	H	4-CH_3O·$C_6H_4CH_2$	1.79	41.28	4.08
2i	H	4-Cl·$C_6H_4CH_2$	1.82	41.42	4.08
2j	H	4-CN·$C_6H_4CH_2$	1.84	42.20	4.20
2k	CH_3O	C_6H_5	1.41	41.99	3.90
2l	CH_3O	4-CH_3·$C_6H_4CH_2$	1.42	41.57	4.06
2m	CH_3O	4-CH_3O·$C_6H_4CH_2$	1.41	41.09	4.07
2n	CH_3O	4-Cl·$C_6H_4CH_2$	1.50	41.09	4.09
2o	CH_3O	4-CN·$C_6H_4CH_2$	1.47	41.68	4.11

Irreversible oxidation in all cases at substrate concentration 2–3 mM, n=0.6 V s^{-1}, CH_3CN–Bu_4NBF_4 (0.1 M), Pt anode (0.5 mm diameter), Ag/$AgNO_3$ (0.1 M). In $CDCl_3$, vs. TMS, at 63 MHz (^{13}C) and 250 MHz (^{1}H).

[a] Calibrated against the reversible redox couple for 9,10-diphenylanthracene (E^0=0.85 V vs. Ag/Ag$^+$, 1.22 V vs. SCE).[13,14]

[b] Ref. 15.

consistent. However, in the radical–cation of the 2-methylnaphthalenes electron donation by the 6-methoxy group does not, by analogy with, e.g. 4-methoxytoluene, apparently promote deprotonation of the side chain to a point where it competes with either radical–cation/radical–cation or radical–cation/substrate dimerisation.

It is appropriate therefore to attempt to assess quantitatively the effect of substituents on the aromatic nucleus and at the side-chain. Oxidation potentials were measured by cyclic voltammetry as a measure of the substituents' influence on radical–cation stability (Table 3). ^{13}C NMR chemical shifts for the 2-CH_2Y carbons in selected compounds of type **2** were also measured as an indicator of the effect of substituents on the polarity of that carbon atom (Table 3).

The results in Table 3 make clear the polar effects of the substituents. As expected, the oxidation potentials are, relative to that of the parent 2-methylnaphthalene, significantly lowered by electron donating substituents at the 6-position and increased by the electron-withdrawing $EtOSO_2$ substituent. Furthermore, the changes in oxidation potential correlate roughly with σ_R^0 (Fig. 1). Similarly, changes in the polarity of the benzylic carbon atom at the 2-position, as measured by ^{13}C chemical shifts, are also demonstrably linked to substitution in the 6-position and

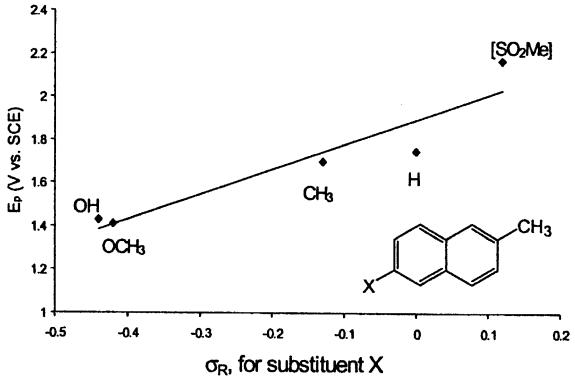


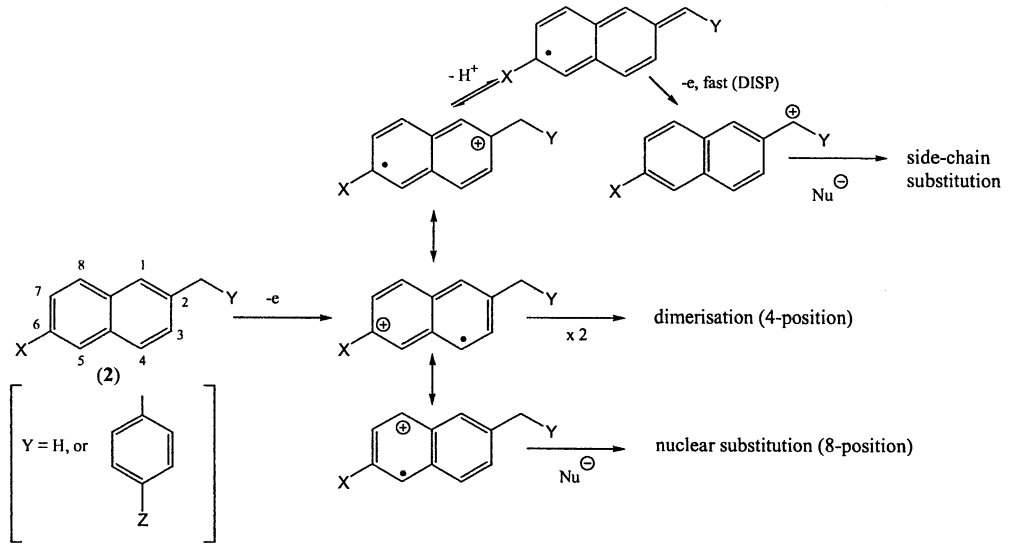
Figure 1. Polar effects on oxidation potentials.

in the 2-ArCH_2 group. The largest shift in ^{13}C chemical shift is caused by the change from 2-CH_3 to 2-CH_2Ar, presumably a consequence of the electronegative sp^2 carbon of the phenyl group. Within the range of compounds **2f**–**2j** the 4-CN group causes a relatively small downfield shift ($\Delta\delta$=0.06 ppm) whereas 4-MeO causes a larger upfield shift ($\Delta\delta$=0.86 ppm).

However, these are initial state effects and it is not clear what the polar effect would be on the stability of the doubly benzylic radical formed by deprotonation of the benzylic protons in the radical–cations of compounds **2f**–**2o**. Such a radical would undoubtedly be stabilised by spin delocalisation but it is not obvious whether such stabilisation would be expected to be more or less than that of the parent radical–cation by 6-substitution (**2k**–**2o**). At least for X=H (**2f**–**2j**) it is possible that stabilisation of the doubly benzylic radical, by spin delocalisation, would enhance deprotonation of the radical–cation—see Scheme 1 (Y=Ar).

Within the series X=H and X=OMe the E_p values for oxidation are essentially unaffected by substitution in the remote 2-ArCH_2 group (Table 3) as shown by the results for compounds **2f**–**2o**. Substitution in the 2-ArCH_2 group does not, therefore, relay its ground state electronic effect to the naphthalene nucleus despite having a profound effect at the benzylic carbon. For the plot in Fig. 1, σ_R^0 values, derived[16] from ^{13}C chemical shifts in substituted benzenes, were used and gave a rough but discernible correlation of the data.

The conclusion from these data is that we may expect to enhance the acidity of the benzylic protons in the radical–cations bearing the 2-($CH_2C_6H_4$·Z-4) group, by virtue of stabilisation by spin delocalisation of the resulting doubly benzylic radical and to fine-tune it by substitution at the 4-position. However, unlike the 4-methoxytoluene radical–cation case, side-chain deprotonation may face severe competition from the dimerisation and nuclear substitution pathways. In any event, the predictions concerning the effects of the different types of substitution on the



Scheme 1.

competition between side-chain and nuclear nucleophilic substitution and dimerisation need testing by experiment.

1.4. Anodic oxidation of 2-CH_2Ar substituted naphthalenes

Key results from constant current preparative-scale electrolysis of a selection of 2-CH_2Ar substituted analogues are summarised in Table 4. The preparative outcome is disappointing. A much lower current density (and a larger anode to compensate) was used in an attempt to suppress dimerisation. This appeared to be effective, but nuclear substitution was preferred except for the 2-(4-methoxybenzyl) derivative (**2h**) where a low yield of side-chain methoxylated product (**14**) was obtained.

1.5. Side chain substitution via DDQ oxidation

2-Methoxy-6-methylnaphthalene (**2d**) is oxidised to 2-methoxy-6-naphthalene carboxaldehyde in 90% yield by DDQ in acetic acid solution whereas 2-methylnaphthalene does not react under the same conditions.[17] Consequently, a systematic exploration was undertaken of the reactions between DDQ and the series of 2- and 6-substituted naphthalenes, as a comparison between a chemical oxidant and the electrochemical alternative. Key results are summarised in Table 5.

Table 4. Preparative anodic oxidation of 2-CH_2Ar substituted naphthalenes

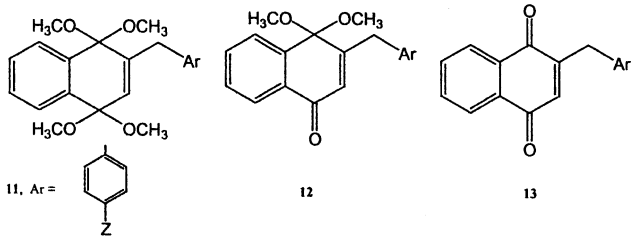
Substrate (4-Z)	Products (%)[a]				Σ	Conversion (%)
	Nuclear			Side-chain		
	11	**12**	**13**	**14**		
2f (H)	6	–	54	–	60	92
2g (CH_3)	5	6	32	–	43	90
2h (CH_3O)	–	–	–	12	12	>95
2i (Cl)	–	31	9	–	40	>95
2k–2o	Intractable oils[b]					

Substrate concentration 0.05 M, divided cell, Pt plate anode (6.25 cm^2), carbon rod cathode, constant current (6.4 mA cm^{-2}, 8 F), MeOH–CH_2Cl_2 (10% v/v) –KF (0.2 M).

[a] Isolated yield.

[b] ^1H NMR of the crude product indicated traces of naphthoquinones. For an electrolysis in MeOH–CH_2Cl_2–H_2SO_4 solution (see Table 2) some coupling products (<5%) were evident but not isolated.

Side-chain oxidation by DDQ is efficient where an electron-donating substituent is present at the 6-position. Furthermore, products at a lower level of oxidation (e.g. **2p** and **2q**) are converted smoothly into the 2-carboxaldehydes. The parent 2-methylnaphthalene and compound **2e**, with the strongly electron-withdrawing $EtO{\cdot}SO_2$ substituent, do not react with DDQ under the conditions used. A particularly significant finding is the conversion in dry benzene of compound **2d** into the side-chain oxidised DDQ adduct **15**.



1.6. Mechanistic rationalisation

The main facts to be explained concerning the electro-oxidation of 6-substituted-2-alkyl naphthalenes are:

1. Direct side-chain oxidation is not achieved in the 6-substituted-2-methyl series.
2. For electron-rich derivatives that gave identifiable products (2-methoxy-6-methylnaphthalene, **2d**, and 2-methylnaphthalene, **2a**) the main products were the

Table 5. DDQ oxidation of 6-X-2-CH_2Y substituted naphthalenes (**2**)

Substrate			Product (% yield)[a]			Conversion (%)
Compound number	X	Y	DDQ[b]	Reflux (h)	**3** (Y=H)	
2a	H	H	3	18	–	0
2b	CH_3	H	2	4	50[c]	>95
2d	CH_3O	H	3	4	90	>95
2d	CH_3O	H	1	8 days	(**15**, 70%)	–[d]
2p	CH_3O	OH	1.5	4	95	>95
2q	CH_3O	Oac	1.5	4	95	>95
2e	$EtOSO_2$	H	3	4	0	50[e]

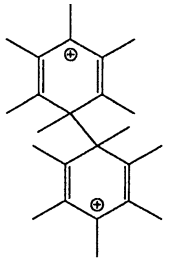
In acetic acid–water (10–15% v/v).
[a] Isolated yields.
[b] Molar equivalents.
[c] A further 30% was a mixture of products hydroxylated at both side-chains.
[d] In dry benzene, overall conversion not measured.
[e] A mixture of hydrolysed sulfonate ester and starting material was obtained.

dimers **9a** and **9b** (23 and 72%, respectively). Dimerisation is suppressed in oxidation of the least electron-rich derivative (ethyl 6-methyl-2-naphthalenesulfonate, **2e**), in which case nuclear substitution is observed to give **10**.

3. In the 2-benzylnaphthalene series, **2f**–**2i**, 4-substitution in the benzyl group does not influence potentials for oxidation of the naphthalene nucleus although ^{13}C chemical shifts indicate that the polarity of the benzylic carbon (C-2) is influenced. However, anodic oxidation of these compounds gives mainly nuclear substitution except for 2-(4-methoxybenzyl)naphthalene (**2h**), which gives a relatively small amount of side-chain oxidation (12%).
4. However, for the relatively electron-rich derivatives (2,6-dimethylnaphthalene, **2b** and 2-methoxy-6-methylnaphthalene, **2d**) efficient side-chain oxidation is achieved by reaction with DDQ in acetic acid. In dry benzene, an adduct (**15**) formed between the substrate and DDQ can be isolated in good yield.

1.7. Direct anodic side-chain oxidation—deprotonation of methylarene radical–cations

Kinetic measurements of the deprotonation of arene radical cations in water[8] and in acetonitrile[18] have been reported, the latter case being in second order reactions with pyridine derivatives. In both examples electron donor substituents cause radical cations derived from electron-rich methylarenes to deprotonate more slowly. In water the radical–cations were formed by irradiation, whereas in acetonitrile they were formed by oxidation with Fe(III) complexes and reacted with pyridine derivatives. In neither case were the benzyl radicals further oxidised to benzyl cations, hence stabilisation of the initial radical–cations by electron donors dominated. In our electrochemical experiments, the benzyl radicals formed by deprotonation of radical–cations are rapidly oxidised further by a second radical cation in homogeneous electron transfer (the DISP mechanism, Scheme 1) and whether or not stabilisation of the benzyl cations encourages deprotonation has to be considered. Certainly for anodic oxidation of toluenes electron donating substituents, especially methoxyl, favour deprotonation in preparative experiments. However, the subsequent oxidation of the benzyl radicals formed by deprotonation should not in principle affect the competition between the rates of deprotonation of the radical–cations vis à vis dimerisation and nucleophilic substitution. For the 2-alkylnaphthalenes side-chain substitution is clearly highly disfavoured in comparison with the alternative pathways, even with 6-methoxyl substitution, probably meaning that stabilisation of the first-formed radical–cation is more important than stabilisation of the neutral benzyl radical. Furthermore, even the possibility of substantial stabilisation by deprotonation to a doubly benzylic radical, as for the 2-arylbenzyl series, does not promote side chain substitution in favour of alternative pathways.



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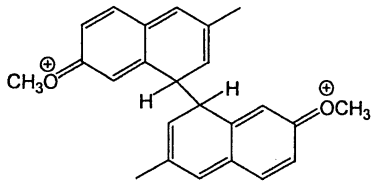

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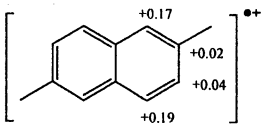

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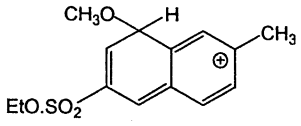

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1.8. Dimerisation vs nuclear substitution

In the 2-methyl-6-X-naphthalenes electron withdrawal at the 6-position (X=$EtOSO_2$) apparently promotes nuclear substitution as opposed to dimerisation and deprotonation. In contrast, stabilisation of the first-formed radical–cation by electron donation (X=MeO, Me) favours dimerisation over the alternative pathways. It is tempting to explain the ready dimerisation in terms of delocalisation of the positive

charge reducing coulombic repulsion between two reacting radical–cations. However, whilst relevant calculations indicating charge density have been carried out (described later) we have no information on the corresponding spin densities that must control dimerisation. A relatively simple view of why dimerisation at the 4-position is favoured is expressed in structure **17**, that of the dihydro intermediate, which shows how the two positive charges are stabilised by the methoxyl groups.

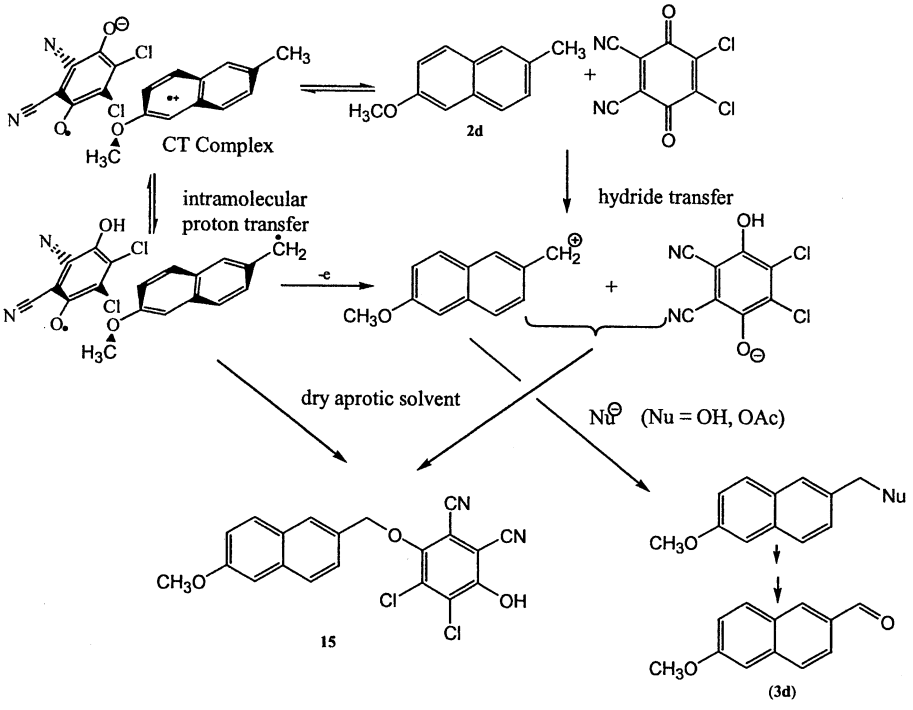
A similar relationship is found for the dimerisation[19,20] of the radical–anions of esters of cinnamic acid. In that case the more easily reduced esters gives rise to radical–anions that dimerise the fastest and in contrast they react with an electrophile (proton) the slowest. In each case the relationship between reduction potential and log *k* (for dimerisation or for protonation) is linear but of opposite slope! A theoretical treatment of this competition has been attempted.[20,21]

Eberson and co-workers[22] calculated atomic charges in a series of methyl-substituted naphthalenes radical–cations. Most relevant for us is the result for 2,6-dimethylnaphthalene, given in structure **18**. The relatively high charge densities at the 1 and 4 positions are consistent for the anodic reaction of **2e** with the observed formation by nucleophilic attack of **10**. After nucleophilic attack on the radical cation subsequent further oxidation would give the intermediate **19** in which the 2-methyl group has a stabilising role.

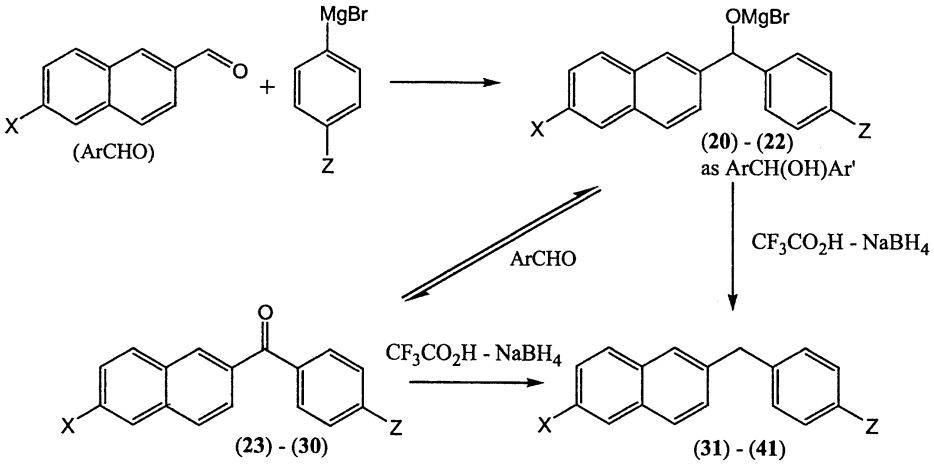
1.9. Oxidation with DDQ

DDQ forms charge transfer (donor–acceptor) complexes (CT), usually highly coloured, with aromatic hydrocarbons. The stability of the complexes is a function[23,24] of the acceptor ability of the quinone, reflected in its reduction potential (0.5 V vs SCE in MeCN[25]) and the donor ability of the aromatic hydrocarbon, reflected in its oxidation potential. Based on this compelling precedent we would expect the formation of relatively stable complexes between DDQ and the more electron rich naphthalene derivatives.

Reaction between DDQ and 2-methyl- or 2-benzylnaphthalenes is relatively fast (4 h) in aqueous acetic acid (at 80°C) and slow (ca. 3 days) in dry benzene. In both cases the initial solutions are dark green, indicating CT complexation, and as reaction proceeds the colour fades. In aqueous acetic acid side-chain oxidation is efficient whereas in dry benzene the adduct **15** is obtained. These observations are consistent with the mechanistic possibilities set out in Scheme 2 for the oxidation of **2d**. It is commonly supposed that DDQ and related oxidations proceed via hydride transfer and that route is included in Scheme 2 for completeness. However, because of the likely formation of CT complexes we also propose that intramolecular deprotonation of the radical–cation of **2d**, in the CT complex, is now facile because the base (the quinone radical–anion) is juxtaposed. In dry aprotic solvent, the radical pair so produced collapses to form the adduct **15**. Otherwise, further electron transfer, presumably from a second molecule of DDQ, produces the benzyl cation leading by side-chain substitution and further similar steps to the aldehyde. The direct hydride transfer route will lead to the same products. It has been shown (Table 5) that the side-chain substituents $-CH_2Nu$ (Nu=OH, OAc) are further oxidised as proposed. Constant potential oxidation of non-stoichiometric mixtures of substrate and DDQ reveals that spent DDQ can be regenerated in situ and efficient side-chain oxidation of electron-rich 2-methyl and 2-benzylnaphthalenes results.[26] These experiments will be described in full elsewhere.



Scheme 2.



Scheme 3.

1.10. The naphthylarylmethane derivatives; routes to starting materials and intermediates

The investigation required the synthesis of several new compounds and the routes used are summarised in Scheme 3. The Grignard addition step gave, in some cases an unexpected result, whereby addition of a Grignard reagent to an aldehyde occurred but the adduct was oxidised by the aldehyde to give a naphthylaryl ketones. This reaction, reminiscent of the Oppenauer oxidation of alcohols by alkoxides, appears to be favoured when the Grignard reagent is electron rich although the pattern is not completely clear.

The conversion of naphthylarylmethanols into the naphthylarylmethanes proceeded efficiently on treatment with sodium borohydride in trifluoroacetic acid. Intense colours were observed, presumably due to intermediate naphthylarylmethyl cations, and these faded as reduction took place. Fortunately the unexpected formation of naphthylaryl ketones did not hamper preparation of the desired naphthylarylmethanes because the ketones could be reduced sequentially by sodium borohydride in trifluoroacetic acid. The reduction was not completely selective in those cases where nitrile substituents were present as competing reduction to amines took place. Full details are given in the Section 2.

2. Experimental

2.1. Electrochemical experiments

Cyclic voltammetric experiments (CV) were performed using a VersaStat EG&G Princeton Applied Research potentiostat with Model 270/250 Research Electrochemistry Software v 4.00.

The cells were equipped with either a platinum bead electrode, which was heated over a Bunsen flame until red-hot between separate runs, or platinum micro disc electrodes with a diameter of 0.5 or 0.75 mm, which were washed with acetone, dried and polished using 'Emery' polishing paper between runs. The counter electrode used was a coiled platinum wire, which was positioned about 0.5 cm from the working electrode. Three different types of reference electrodes were used. An Ag/AgBr electrode was freshly made prior to measurement by electroplating silver bromide onto the surface of a silver wire from a saturated KBr solution by passing current between the silver wire (anode) and a carbon rod (cathode). An Ag/Ag^+ electrode was constructed by inserting a silver wire into an acetonitrile solution containing silver nitrate (0.1 M) that was divided from the bulk solution using 'cracked' glass. These electrodes were calibrated with regard to SCE using the reversible oxidation potential (E^0, first wave) of 9,10-diphenylanthracene as standard after a set of measurements; the E^0 value for 9,10-diphenyl anthracene in acetonitrile/tetrabutylammonium tetrafluoroborate (0.1 M) is known[13,14] to be 0.85 V vs SCE.

The solvents used were normally freshly distilled and kept over freshly activated molecular sieves to ensure dryness. Supporting electrolytes, usually tetraalkylammonium salts, were dried in an oven (~120°C) for at least 24 h or in a reduced pressure oven (~50°C, ~20 mmHg) for 8 h prior to use.

2.2. Controlled potential electrolysis

Preparative scale electrochemical reductions were carried out using a DT 2101 Hi Tek potentiostat with an electronic charge integrator constructed in the Department's electronic workshop. Conventional glass cells were used, typically equipped with either Pt foil or Pt disc anodes and carbon counter electrodes with the anode and cathode compartments separated by a glass sinter for electrolysis in divided cells. The reference electrode was Ag/AgBr positioned as closely as possible to the working electrode. The electrolytes were stirred magnetically and the reaction was kept in an inert atmosphere by the slow bubbling of nitrogen through the solution. Constant temperature conditions were maintained either by using cells with cooling jacket designs or cells immersed in heated oil baths.

2.3. Controlled current electrolysis

To ensure an even current gradient the two-electrodes were

positioned parallel to each other. The distance between the electrodes was large enough for efficient mass transport but close enough to ensure low solution/electrolyte resistance.

2.4. Instruments

^{1}H NMR spectra were recorded either on a Bruker WP-80 (80 MHz), a Bruker AM-250 (250 MHz) or Bruker AMX-600 (600 MHz). Solution ^{13}C NMR spectra were also recorded on the Bruker AM-250 (250 MHz) and the Bruker AMX-600 (600 MHz). Solid state ^{13}C NMR spectra were obtained from the Solid State NMR Service of the ULIRS based at University College London, and recorded on a Bruker MSL-300 (75 MHz). Mass spectra were obtained on a Kratos MS-50RF instrument with a Kratos DS90 data requisition system. Elemental analysis data were obtained from the Elemental Analysis Service at University College London.

UV-HPLC analytical experiments were conducted using a KippAnalytica, 9209 Autosampler connected to a ConstaMetric III pump, feeding a PhaseSep, Spherisorb S5 ODS2 (25 cm×4.6 mm) Reverse phase column. A Spectromonitor III, Model 1204A set at 240 nm, was used as the UV-detector and the chromatograph recorded on a Shimadzu, Chromatopac C-R1B. Flash chromatography was performed using Sorbsil C 40/60H silica gel. Thin layer chromatography was performed using Merck DC-Alufolien Kieselgel 60 F_{254} plates with a thickness of 0.2 mm.

Melting points were measured on a glass slide using a Reichert microscope melting point apparatus. Infrared absorption spectra were recorded on a Perkin–Elmer 1600 series FT-IR spectrometer. Ultraviolet spectra were recorded on a Perkin–Elmer Lambda2 UV/Vis spectrometer.

2.5. Preparation of starting materials

Several substrates and reagents were obtained commercially; 2-methoxy-6-naphthalene carboxaldehyde (**3d**) was a gift from SmithKline Beecham, Worthing.

2.6. Naphthalenes

2.6.1. 2-Methoxy-6-methylnaphthalene (2d). 2-Methoxy-6-naphthalene carboxaldehyde (**3d**) (50.0 g; 0.268 mol) was added in small portions to a stirred mixture containing hydrazine (91 ml; 1.876 mol), KOH (51.7 g; 0.923 mol in diethylene glycol (420 ml). The mixture was heated slowly to near reflux (ca. 165°C) resulting in vigorous gas evolution (N_2). After 22 h the pale green slurry was allowed to cool and poured into stirred ice-water (600 ml) yielding a white precipitate which was stirred for an additional hour. The white precipitate was recrystallised from acetone, filtered and dried in vacuo yielding the title compound (39.7 g; 0.23 mol; 86%) as white micro-needles, mp 75–76°C (lit.,[27] 76°C). UV (MeCN): λ (ε, dm^3 mol^{-1} cm^{-1})=228 (27,800), 260 (4400), 333 nm (1900). ^{1}H NMR (250 MHz, $CDCl_3$):δ=2.45 (s, 3H, Ar-C*H*$_3$), 3.86 (s, 3H, Ar-OC*H*$_3$), 7.08–7.12 (m, 2H, Ar-*H*), 7.25 (dd, 1H, *J*=8.4, 1.7 Hz, Ar-*H*), 7.50 (d, 1H, *J*=0.8 Hz, Ar-*H*), 7.62 (d, 1H, *J*=7.3 Hz, Ar-*H*), 7.63 (d, 1H, *J*=6.4 Hz, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.54, 55.35, 105.82, 118.73, 126.71, 126.82, 128.69, 128.83, 129.31, 132.81, 133.12, 157.18.

2.6.2. 2-Methyl-6-naphthol (2c). 2-Methoxy-6-methylnaphthalene (**2d**) (5.0 g; 0.029 mol) was dissolved in dry dichloromethane (80 ml) under nitrogen. Boron tribromide (2.0 ml; 20 mmol) was added with a syringe while stirring. The solution was refluxed for 2 h and allowed to cool to room temperature. An aqueous solution of 2 M NaOH (100 ml) was added dropwise and stirred vigorously for 30 min. The organic layer was separated off and the aqueous phase was made acidic with conc. HCl. The aqueous mother liquor was extracted with dichloromethane (3×40 ml). The organic phases were combined and washed firstly with water (5×100 ml) in order to remove H_3BO_3, and then with sat. sodium bicarbonate (2×50 ml). The organic phase was dried over $MgSO_4$ and filtered. The solvent was evaporated off and the remaining brown residue recrystallised from chloroform yielding a dark pink precipitate. After filtration the solid was recrystallised from absolute ethanol yielding a rose-white precipitate which was filtered and dried in vacuo yielding the title compound (4.53 g; 0.286 mol; 98%) as white powder, mp 118–123°C IR (KBr) (cm^{-1}): 3284, 3045, 2941, 1606, 1390, 1208, 1175, 862, 821, 811, 648. UV (MeCN): λ (ε, dm^3 mol^{-1} cm^{-1})231 (30,500), 273 (5300), 336 nm (2500). ^{1}H NMR (250 MHz, CD_2Cl_2): δ=2.47 (s, 3H, Ar-C*H*$_3$), 5.89 (br. s, 1H, Ar-O*H*), 7.06–7.13 (m, 2H, Ar-*H*), 7.28 (dd, 1H, *J*=8.4, 1.7 Hz, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 7.58 (d, 2H, *J*=8.5 Hz, Ar-*H*), 7.66 (d, 1H, *J*=8.7 Hz, Ar-*H*). ^{13}C NMR (63 MHz, CD_2Cl_2): δ=21.93, 110.04, 118.52, 126.91, 127.43, 129.55, 129.82, 129.88, 133.57, 133.91, 153.74. MS; *m*/*z* (%)=158.1 (M$^+$, 100), 141.1 (3), 128.1 (9), 115.0 (2). MS; *m*/*z*, M$^+$ 158.0735 (calcd for $C_{11}H_{10}O$ 158.07317).

2.6.3. Sodium 6-methyl-2-naphthyl sulfonate, (sodium menasylate). 2-Methylnaphthalene (**2a**) (76.0 g; 0.53 mol) was heated until it melted (40°C) and *conc*. H_2SO_4 (98%; 76.0 g; 40 ml) was added slowly to the stirred suspension. The temperature rose to 140°C during the addition and was kept between 90 and 120°C for an additional 6 h. The dark blue slurry was poured into ice-cold water (300 ml). By-products were extracted and separated off with benzene (2×50 ml) and the aqueous phase was added to a sat. NaCl solution (500 ml) resulting in an off-white precipitation. The slurry was additionally stirred for 16 h and then cooled to about 5°C. After filtration the grey clay was dried in vacuo at 140°C until dry. The solid was suspended in acetone (300 ml) and stirred vigorously for 1 h. The dark blue slurry was filtered and the solid was then recrystallised twice from water (2×1000 ml). The precipitate was filtered and dried in vacuo yielding the title compound (69.0 g; 53%) as grey micro-crystals, mp>340°C (lit.,[28] >280°C). IR (KBr) (cm^{-1}): 3054, 1219, 1136, 1102, 1041, 894, 830, 740, 700, 656, 616. ^{1}H NMR (250 MHz, D_2O): δ=2.52 (s, 3H, Ar-C*H*$_3$), 7.48 (dd, 1H, *J*=8.4, 1.5 Hz, Ar-*H*), 7.72 (s, 1H, Ar-*H*), 7.83 (dd, 1H, *J*=8.7 Hz, *J*=1.8 Hz, Ar-*H*), 7.91 (d, 1H, *J*=8.3 Hz, Ar-*H*), 7.93 (d, 1H, *J*=8.7 Hz, Ar-*H*), 8.33 (s, 1H, Ar-*H*).

2.6.4. 6-Methyl-2-naphthalene sulfonic acid, (menasylic acid). Sodium 6-methyl-2-naphthalene sulfonate (6.0 g;

28.3 mmol) was heated until reflux for 3 h in 2N HCl (40 ml) and allowed to cool slowly to room temperature. The grey solid was filtered off and recrystallised from ethyl acetate (35 ml). The precipitate was filtered and dried in vacuo yielding the title compound (5.97 g; 26.9 mmol; 95%) as colourless crystals, mp 125–128°C (lit.,[28] 118–121°C). IR (KBr) (cm^{-1}): 3323, 3034, 1376, 1200, 1105, 1032, 892, 825, 739, 700, 658, 614. ^{1}H NMR (250 MHz, D_2O): δ=2.52 (s, 3H, Ar-CH_3), 7.48 (dd, 1H, J=8.4, 1.5 Hz, Ar-*H*), 7.72 (s, 1H, Ar-*H*), 7.83 (dd, 1H, J=8.7, 1.8 Hz, Ar-*H*), 7.91 (d, 1H, J=8.3 Hz, Ar-*H*), 7.93 (d, 1H, J=8.7 Hz, Ar-*H*), 8.33 (s, 1H, Ar-*H*). MS; *m/z* (%)=222.0 (M^+, 100), 141.1 (32), 115.1 (12), 113.0 (44). MS; *m/z*, M^+ 222.0359 (calcd for $C_{11}H_{10}O_3S$ 222.0055).

2.6.5. 6-Methyl-2-naphthalene sulfonic chloride. 6-Methyl-2-naphthalene sulfonic acid (21.37 g; 0.088 mol) was dissolved in stirred dimethyl formamide (100 ml) under nitrogen. Thionyl chloride (10 ml) was added dropwise at room temperature and stirred for 30 min. The mixture was poured into ice-water yielding a grey precipitate which was filtered and dried in vacuo yielding the title compound (18.14 g; 0.0754 mol; 86%) as grey powder, mp 98–99°C (lit.,[28] 98–99°C).

2.6.6. Ethyl 6-methyl-2-naphthalene sulfonic ester (2e). 6-Methyl-2-naphthyl sulfonyl chloride (15.0 g; 0.062 mol) was added in small portions to an ice-cold stirred solution containing absolute ethanol (20 ml) and pyridine (10 g). The mixture was stirred for 3 h and then quenched with aqueous 2 M HCl for 1 h yielding a white precipitate which was filtered and dried in vacuo yielding the title compound (8.60 g; 0.034 mol; 55%) as white micro-crystals, mp 65–70°C. Anal. calcd for $C_{13}H_{14}O_3S$: C, 62.39%; H, 5.64%. Found C, 62.56%; H, 5.71%. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=228 (35,000), 280 (5300), 325 nm (900). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.28 (t, 3H, J=7.1 Hz, –CH_2–CH_3), 2.53 (s, 3H, Ar-CH_3), 4.14 (q, 2H, J=7.1 Hz, –CH_2–CH_3), 7.43 (dd, 1H, J=8.4, 1.5 Hz, Ar-*H*), 7.66 (s, 1H, Ar-*H*), 7.82–7.88 (m, 3H, Ar-*H*), 8.43 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, CD_3CN): δ=14.80, 21.98, 67.04, 122.70, 127.06, 128.94, 129.13, 129.42, 130.14, 130.28, 132.26, 135.82, 139.75. MS; *m/z* (%)=250.1 (M^+, 100), 222.0 (78), 141.1 (41), 129.1 (8), 115.1 (18). MS; *m/z*, M^+ 250.0664 (calcd for $C_{13}H_{14}O_3S$ 250.06637).

2.7. Naphthyl phenyl ketones and methanols

2.7.1. 2-Naphthyl phenyl methanol (20). To a stirred solution containing magnesium turnings (1.46 g; 0.06 mol) in 50 ml dry diethyl ether, about a third of the required bromobenzene (9.42 g; 0.06 mol) was added. When reaction was under way the remaining bromobenzene was added in a rate governed by the resulting effervescence. A solution of 2-naphthalene carboxaldehyde (**3a**) (6.5 g; 0.04 mol) in 100 ml diethyl ether was added dropwise, and the resulting slurry was allowed to react for 20 h at room temperature. The mixture was then quenched with cold aqueous 2 M HCl (400 ml) for 1 h while stirring. After extraction into diethyl ether (3×60 ml), the separated organic layers were combined and washed with saturated sodium carbonate (100 ml). The organic layer was dried over anhydrous magnesium sulfate for 3 h. After filtration the diethyl ether was evaporated off, giving a crude brown oil which was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (7.36 g; 76%) as white micro-crystals, mp 84–86°C (lit.,[29] 86–87°C).

2.7.2. 2-Naphthyl 4-methylphenyl ketone (25). A Grignard reagent was generated from 2-bromonaphthalene (7.25 g; 0.035 mol) as previously described. A solution of 4-methylbenzaldehyde (8.4 g; 0.07 mol; 2 equiv.) in 50 ml dry diethyl ether was added dropwise, and the resulting slurry was allowed to react for 20 h at room temperature. The mixture was then quenched with cold aqueous 2 M HCl (500 ml) for 2 h while stirring. After extraction into diethyl ether (3×70 ml), the separated organic layers were combined and washed with saturated sodium carbonate (100 ml). The organic layer was dried over anhydrous magnesium sulfate for 3 h. After filtration the diethyl ether was evaporated off, giving a crude brown oil which was distilled. The fraction containing 4-methyl benzyl-alcohol (3.5 g; bp 110°C/~15 mmHg) was taken off, and the remaining residue was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (5.6 g; 65%) as off-white crystals, mp 87–89°C. Anal. calcd for $C_{18}H_{14}O$: C, 87.77%; H, 5.73%. Found C, 87.83%; H, 5.71%. IR (KBr) (cm^{-1}): 3048, 2917, 1661, 1590, 1254, 1078, 1033, 845, 820, 773, 753. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=219 (52,000), 255 (37,000), 303 nm (12,000). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.46 (s, 3H, –CH_3), 7.31 (dd, 2H, J=8.4, 1.6 Hz, Ar-*H*), 7.54 (td, 1H, J=6.7, 1.5 Hz, Ar-*H*), 7.60 (td, 1H, J=6.7, 1.5 Hz, Ar-*H*), 7.78 (dd, 2H, J=6.5, 1.6 Hz, Ar-*H*), 7.88–7.94 (m, 4H, Ar-*H*), 8.25 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.73, 125.92, 126.60, 127.88, 128.24, 129.10, 129.42, 130.41, 131.60, 132.36, 135.28, 143.24, 196.52. MS; *m/z* (%)=246.1 (M^+, 98), 231.1 (12), 127.1 (46), 119.1 (100). MS; *m/z*, M^+ 246.1046 (calcd for $C_{18}H_{14}O$ 246.1045).

2.7.3. 2-Naphthyl 4-methoxyphenyl ketone (26). To a stirred solution containing magnesium turnings (0.60 g; 0.025 mol) in 80 ml dry diethyl ether, about a third of the required Grignard reagent, prepared in dry diethyl ether from 2-bromonaphthalene (5.00 g; 0.024 mol), was reacted with a solution of 4-methoxybenzaldehyde (**3f**) (6.6 g; 0.05 mol; 2 equiv.) as described above. Work up as before gave a crude brown oil which was distilled. The fraction containing 4-methoxy benzylalcohol (3.2 g; bp 142–145°C/~15 mmHg) was taken off, and the remaining residue was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (4.9 g; 64%) as off-white crystals, mp 89–90°C (lit.,[30] 91–93°C).

2.7.4. 2-Naphthyl 4-chlorophenyl ketone (27). Reaction between the Grignard reagent from 2-bromonaphthalene (9.5 g; 0.045 mol) and 4-chlorobenzaldehyde (6.4 g; 0.045 mol) in 70 ml dry tetrahydrofuran gave a crude brown oil which was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (4.8 g; 41%) as off-white crystals, mp 122–124°C. Anal. calcd for $C_{17}H_{11}OCl$: C, 76.55%; H, 4.16%. Found C, 77.01%; H, 4.20%. IR (KBr)

(cm^{-1}): 3050, 1654, 1586, 1278, 1088, 846, 819, 774, 756. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=218 (51,400), 254 (35,900), 334 nm (1700). ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.47–7.66 (m, 4H, Ar-*H*), 7.79–7.84 (m, 2H, Ar-*H*), 7.88–7.98 (m, 4H, Ar-*H*), 8.24 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=125.60, 126.95, 127.89, 128.50, 128.72, 129.44, 131.49, 131.73, 132.29, 134.54, 135.37, 136.24, 138.87, 195.50. MS; *m/z* (%)=266.0 (M^+, 32), 231.1 (12), 155.0 (53), 113.0 (100). MS; *m/z*, M^+ 266.0496 (calcd for $C_{17}H_{11}OCl$ 266.0498).

2.7.5. 2-Naphthyl 4-cyanophenyl ketone (28). Similar reaction between 2-bromonaphthalene (14.5 g; 0.07 mol) and 4-cyanobenzaldehyde (9.2 g; 0.07 mol) in 70 ml dry tetrahydrofuran gave a crude brown oil which was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (4.3 g; 17%) as off-white crystals, mp 96–99°C. IR (KBr) (cm^{-1}): 3056, 2230, 1654, 1623, 1280, 824, 776, 764, 700. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=222 (56,100), 253 (41,400), 295 nm (11,900). ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.53–7.68 (m, 2H, Ar-*H*), 7.79–7.99 (m, 8H, Ar-*H*), 8.21 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=115.73, 118.08, 125.32 126.95, 127.23, 127.73, 127.82, 127.96, 128.83, 128.96, 129.59, 130.32, 132.29, 133.71, 135.67, 141.68, 195.06. MS; *m/z* (%)=257.1 (M^+, 18), 155.0 (44), 127.1 (48), 104.0 (100). MS; *m/z*, M^+ 257.0840 (calcd for $C_{18}H_{11}NO$ 257.0841).

2.7.6. 2-(6-Methoxy)-naphthyl phenyl methanol (21). Reaction between the Grignard reagent prepared from bromobenzene (9.42 g; 0.06 mol) and 6-methoxy-2-naphthalene carboxaldehyde (**3d**) (10.0 g; 0.05 mol) in 150 ml diethyl ether gave a crude brown oil which was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (9.53 g; 72%) as white micro-crystals, mp 71–73°C. IR (KBr) (cm^{-1}): 3356, 3057, 1631, 1605, 1483, 1166, 1028, 749, 700. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=232 (52,500), 262 (5600), 330 nm (1500). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.43 (d, 1H, *J*=1.9 Hz, –CH–O*H*), 3.89 (s, 3H, –O*CH*$_3$), 5.94 (s, 1H, –*CH*–OH), 7.09–7.15 (m, 2H, Ar-*H*), 7.24–42 (m, 6H, Ar-*H*), 7.68 ('t', 2H, *J*=8.0 Hz, Ar-*H*), 7.77 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=55.30, 76.32, 105.79, 118.93, 125.04, 125.36, 126.67, 127.19, 127.54, 128.48, 128.71, 129.53, 134.06, 139.01, 143.84, 157.81. MS; *m/z* (%)=264.1 (M^+, 100), 215.1 (9), 185.1 (23), 159.1 (89). MS; *m/z*, M^+ 264.1151 (calcd for $C_{18}H_{16}O_2$ 264.1150).

2.7.7. 2-(6-Methoxy)-naphthyl 4-methylphenyl methanol (22). Reaction between the Grignard reagent prepared form 4-methyl bromobenzene (12.0 g; 0.07 mol) and 6-methoxy-2-naphthalene carboxaldehyde (**3d**) (10.0 g; 0.05 mol) in 100 ml diethyl ether gave a crude yellow solid which was recrystallised from ethanol–isopropyl alcohol. The precipitate was filtered and dried in vacuo yielding the title compound (11.6 g; 84%) as white micro-crystals, mp 88–90°C. IR (KBr) (cm^{-1}): 3312, 2905, 1606, 1508, 1264, 1164, 1030, 859, 816, 773. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=232 (42,400), 262 (8000), 331 nm (1600). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.27 (d, 1H, *J*=3.4 Hz, –CH–O*H*), 2.32 (s, 3H, –*CH*$_3$), 3.89 (s, 3H, –O*CH*$_3$), 5.92 (d, 1H, *J*=2.8 Hz, –*CH*–OH), 7.09–7.15 (m, 4H, Ar-*H*), 7.27 (t, 2H, *J*=8.0 Hz, Ar-*H*), 7.37 (dd, 1H, *J*=8.5, 1.7 Hz, Ar-*H*), 7.68 (t, 2H, *J*=8.0 Hz, Ar-*H*), 7.78 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.07, 55.28, 76.18, 105.78, 118.88, 124.70, 125.36, 126.64, 127.13, 128.72, 129.17, 129.52, 134,02, 137.28, 139.15, 140.99, 157.76. MS; *m/z* (%)=278.1 (M^+, 100), 215.1 (13), 185.1 (85), 159.1 (67). MS; *m/z*, M^+ 278.1308 (calcd for $C_{19}H_{18}O_2$ 278.1307).

2.7.8. 2-(6-Methoxy)-naphthyl 4-methoxyphenyl ketone (24). Similar reaction between 4-methoxy-bromobenzene (13.0 g; 0.07 mol) and 6-methoxy-2-naphthalene carboxaldehyde (**3d**) (10.0 g; 0.05 mol) in 150 ml dry tetrahydrofuran gave a brown solid which was recrystallised from ethanol–isopropyl alcohol and then further purified through silica gel (grade 40–60) using $CHCl_3$ as eluent. Evaporation of the R_f=0.4 fractions and drying in vacuo yielded the title compound (2.2 g; 15%) as white crystals, mp 149–152°C (lit.,[31] 144.5–146°C).

2.7.9. 2-(6-Methoxy)-naphthyl 4-chlorophenyl ketone (29). 6-Methoxy-2-bromo naphthalene (3.00 g; 0.0126 mol) and 4-chloro-benzaldehyde (1.83 g; 0.013 mol) in 20 ml dry tetrahydrofuran were reacted together via the Grignard reagent to give a brown oil which was recrystallised from ethanol–isopropyl alcohol. The title compound (1.4 g; 37%) was obtained as pale yellow crystals, mp 148–150°C. IR (KBr) (cm^{-1}): 3447, 2926, 1649, 1622, 1282, 1214, 863, 842, 816, 747. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=227 (39,900), 263 (33,700), 316 nm (13,500). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.96 (s, 3H, –O*CH*$_3$), 7.19–7.26 (m, 2H, Ar-*H*), 7.46–7.52 (m, 2H, Ar-*H*), 7.77–7.84 (m, 3H, Ar-*H*), 7.88–7.94 (m, 2H, Ar-*H*), 8.17 (s, 1H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=55.52, 105.89, 119.92, 126.42, 127.21, 128.69, 129.56, 131.08, 131.33, 131.43, 131.91, 132.43, 136.59, 137.18, 138.61, 159.91, 195.33. MS; *m/z* (%)=296.1 (M^+, 100), 185.1 (84), 157.1 (19), 114.0 (15). MS; *m/z*, M^+ 296.0598 (calcd for $C_{18}H_{13}O_2Cl$ 296.0604).

2.7.10. 2-(6-Methoxy)-naphthyl 4-cyanophenyl ketone (30). Similar reaction between 6-methoxy-2-bromonaphthalene (9.5 g; 0.04 mol) and 4-cyanobenzaldehyde (9.2 g; 0.07 mol) gave the title compound (4.3 g; 38%) as off-white crystals, mp 125–128°C. Anal. calcd for $C_{19}H_{13}NO_2$: C, 79.42%; H, 4.56%; N, 4.88%. Found C, 79.85%; H, 4.72%; N, 4.89%. IR (KBr) (cm^{-1}): 3056, 2234, 1652, 1621, 1480, 1296, 1282, 1214, 1137, 1016, 874, 850, 803, 764, 710. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=236 (44,800), 320 nm (14,200). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.96 (s, 3H, –O*CH*$_3$), 7.16–7.26 (m, 2H, Ar-*H*), 7.73–7.94 (m, 7H, Ar-*H*), 8.14 (d, 1H, *J*=1.4 Hz, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=55.52, 105.94, 115.41, 118.11, 120.12, 126.08, 127.44, 127.58, 129.66, 130.14, 131.16, 131.52, 132.19, 132.32, 137.48, 142.03, 160.20, 194.78. MS; *m/z* (%)=287.1 (M^+, 100), 185.1 (89), 157.1 (22), 113.0 (28). MS; *m/z*, M^+ 287.0942 (calcd for $C_{19}H_{13}NO_2$ 287.0946).

2.8. Preparation of substituted benzylnaphthalenes

General reduction method. To magnetically stirred trifluoroacetic acid (50 ml) at 0°C under nitrogen, sodium

borohydride (2.0 g; 53 mmol) was carefully added in portions over 45 min. To this slurry a solution of substrate (typically 10 mmol) in dry dichloromethane (40 ml) was added dropwise. As each drop of solution comes in contact with the slurry, a strong colouration (the carbocation) was observed which rapidly disappears. The rate of addition is governed by the rate of colour discharge. After the mixture was stirred at room temperature under nitrogen for typically 20 h, it was quenched with ice cooled aqueous 2 M sodium chloride until alkaline. After extraction into dichloromethane (3×60 ml), the separated organic layers were combined and washed with saturated sodium carbonate (100 ml). The organic layer was dried over anhydrous magnesium sulfate for 3 h. After filtration the dichloromethane was evaporated off, giving a crude solid which was recrystallised from ethanol or propan-2-ol.

2.8.1. 2-Benzylnaphthalene (31). 2-Naphthyl phenyl methanol (**20**) (2.34 g; 10 mmol) was treated according to the general reduction method. The title compound was obtained (1.85 g; 85%) as opaque crystals, mp 34–37°C (lit.,[32] 35.5°C).

2.8.2. 2-(4-Methylbenzyl)-naphthalene (36). 2-Naphthyl 4-methylphenyl ketone (**25**) (2.46 g; 10 mmol) was treated according to the general reduction method to the title compound (2.13 g; 92%) as pale yellow crystals, mp 53–56°C (lit.,[33] 54–56°C).

2.8.3. 2-(4-Methoxybenzyl)-naphthalene (37). 2-Naphthyl 4-methoxyphenyl ketone (**26**) (1.22 g; 4.65 mmol) was treated according to the general reduction method. The precipitate was filtered and dried in vacuo yielding the title compound (1.09 g; 95%) as green metallic plates, mp 58–60°C (lit.,[34] 57–58°C).

2.8.4. 2-(4-Chlorobenzyl)-naphthalene (38). 2-Naphthyl 4-chlorophenyl ketone (**27**) (2.67 g; 10 mmol) was treated according to the general reduction method to give the title compound (2.48 g; 98%) as off-white crystals, mp 47–50°C (lit.,[33] 50–51°C).

2.8.5. 2-(4-Cyanobenzyl)-naphthalene (39). 2-Naphthyl 4-cyanophenyl ketone (**28**) (2.57 g; 10 mmol) was treated according to the general reduction method to give a crude product that was purified by chromatography through silica gel (grade 40–60) using $CHCl_3$ as eluent. Evaporation of the R_f=0.8 fractions and drying in vacuo yielded the title compound (1.5 g; 63%) as white crystals, mp 115–118°C (lit.,[33] 111–114°C).

2.8.6. 6-Methoxy-2-benzylnaphthalene (33). 2-(6-Methoxy)-naphthyl phenyl methanol (**21**) (2.64 g; 10 mmol) was treated according to the general reduction method to the title compound (2.35 g; 95%) as white micro-crystals, mp 88–91°C. Anal. calcd for $C_{18}H_{16}O$: C, 87.06%; H, 6.50%. Found C, 87.15%; H, 6.57%. IR (KBr) (cm^{-1}): 2929, 1605, 1387, 1265, 1227, 1174, 1029, 855, 813, 742, 702. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=230 (27,000), 260 (3000), 320 nm (1200). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.90 (s, 3H, $-OCH_3$), 4.10 (s, 2H, Ar-CH_2-Ar), 7.09–7.31 (m, 8H, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 7.65 (d, 2H, *J*=8.3 Hz, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=41.99, 55.36, 105.81, 118.72, 126.14, 127.02, 128.52, 129.07, 133.19, 136.35, 141.30, 157.41. MS; *m*/*z* (%)=248.1 (M^+, 100), 217.1 (12), 171.1 (8). MS; *m*/*z*, M^+ 248.1202 (calcd for $C_{18}H_{16}O$ 248.1201).

2.8.7. 2-(4-Methylbenzyl)-6-methoxy-naphthalene (34). 2-(6-Methoxy)-naphthyl 4-methylphenyl methanol (**22**) (2.78 g; 10 mmol) was treated according to the general reduction method to give the title compound (2.38 g; 91%) as greenish plates, mp 99–102°C. IR (KBr) (cm^{-1}): 3000, 2919, 1625, 1601, 1472, 1261, 1226, 1026, 850, 808, 791, 738. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=235 (24,000), 261 (5900), 335 nm (1500). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.31 (s, 3H, $-CH_3$), 3.89 (s, 3H, $-OCH_3$), 4.06 (s, 2H, Ar-CH_2-Ar), 7.06–7.13 (m, 6H, Ar-*H*), 7.26 (dd, 1H, *J*=8.4, 1.7 Hz, Ar-*H*), 7.54 (s, 1H, Ar-*H*), 7.61–7.67 (m, 2H, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.07, 41.57, 55.35, 105.84, 118.74, 126.97, 128.20, 128.94, 129.10, 129.21, 133.19, 135.62, 136.66, 138.25, 157.39. MS; *m*/*z* (%)=262.1 (M^+, 100), 247.1 (20), 113.0 (46). MS; *m*/*z*, M^+ 262.1358 (calcd for $C_{19}H_{18}O$ 262.1358).

2.8.8. 2-(4-Methoxybenzyl)-6-methoxy naphthalene (35). 2-(6-Methoxy)-naphthyl 4-methoxyphenyl ketone (**24**) (1.46 g; 5 mmol) was treated according to the general reduction method to give the title compound (1.18 g; 85%) as white micro-crystals, mp 95–96°C (lit.,[35] 103–104°C).

2.8.9. 2-(4-Chlorobenzyl)-6-methoxy naphthalene (40). 2-(6-Methoxy)-naphthyl 4-chlorophenyl ketone (**29**) (0.21 g; 0.7 mmol) was treated according to the general reduction method to give the title compound (0.18 g; 90%) as off-white micro-crystals, mp 96–98°C. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=233 (31,200), 260 nm (6700), 331 nm (1700). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.90 (s, 3H, $-OCH_3$), 4.09 (s, 2H, Ar-CH_2-Ar), 6.87 (dd, 2H, *J*=6.6, 2.1 Hz, Ar-*H*), 7.10–7.19 (m, 4H, Ar-*H*), 7.24 (dd, 1H, *J*=9.2, 1.8 Hz, Ar-*H*), 7.57 (s, 1H, Ar-*H*), 7.69 (dd, 2H, *J*=10.2, 1.8 Hz, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=41.09, 55.34, 105.83, 114.00, 116.71, 126.87, 126.94, 127.77, 128.23, 129.32, 130.11, 132.32, 133.19, 133.39, 136.85, 157.46, 158.13. MS; *m*/*z* (%)=282.1 (M^+, 100), 251.1 (10), 216.1 (16), 171.1 (6), 113.0 (7). MS; *m*/*z*, M^+ 282.0810 (calcd for $C_{18}H_{15}OCl$ 282.0811).

2.8.10. 2-(4-Cyanobenzyl)-6-methoxy-naphthalene (41). 2-(6-Methoxy)-naphthyl 4-cyanophenyl ketone (**30**) (2.87 g; 10 mmol) was treated according to the general reduction method to give a crude product, which was purified by chromatography through silica gel (grade 40–60) using $CHCl_3$ as eluent. Evaporation of the R_f=0.7 fractions and drying in vacuo yielded the title compound (0.5 g; 19%) as white crystals, mp 109–111°C. IR (KBr) (cm^{-1}): 3011, 2936, 2226, 1604, 1481, 1259, 1112, 1032, 813, 699. UV (MeCN): λ (ε, $dm^3\,mol^{-1}\,cm^{-1}$)=244 (33,000), 262 (12,000), 335 nm (2700). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.88 (s, 3H, $-OCH_3$), 4.11 (s, 2H, Ar-CH_2-Ar), 7.09–7.22 (m, 3H, Ar-*H*), 7.27 (d, 2H, *J*=8.2 Hz, Ar-*H*), 7.51 (s, 1H, Ar-*H*), 7.52 (d, 2H, *J*=8.2 Hz, Ar-*H*), 7.65 (dd, 2H, *J*=8.4, 3.9 Hz, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=41.68, 55.08, 105.62, 118.90, 127.05, 127.16 127.61, 128.88, 129.47, 132.03, 133.22, 134.32, 146.66, 157.47. MS; *m*/*z* (%)=273.1 (M^+, 100), 230.1 (10), 171.1

(10). MS; *m/z*, M^+ 273.1154 (calcd for $C_{19}H_{15}NO$ 273.1154).

2.9. Preparative scale electrolyses of substituted toluenes

General procedure for controlled current electrolyses. Dry potassium fluoride (0.22 g; 3.8 mmol) was added to 25 ml of freshly distilled methanol in an undivided cell equipped with a magnetic stirrer and nitrogen inlet. The substrate (typically 17.5 mmol) was then added and electrolysis carried out at constant current (64 mA cm^{-2}). The solution slowly turned pale yellow, and hydrogen evolution was observed at the counter electrode. The reaction was terminated after the passage of 4.2 F. The solvents were evaporated. The yellow oily residue obtained was quenched with 170 ml water, and then extracted into 150 ml diethyl ether. After separating off the aqueous layer, the organic layer was washed thoroughly with saturated sodium carbonate solution (3×70 ml). The separated ether layer was then dried ($MgSO_4$). After filtration through celite the solvent was evaporated off. The orange residue obtained was then distilled under reduced pressure (~10 mmHg).

2.9.1. Electrochemical oxidation of 4-methyltoluene (1b). 4-Methyltoluene (**1b**, 1.86 g; 17.5 mmol) was treated according to the general method given above. The orange residue (2.5 g) obtained was distilled under reduced pressure (10 mmHg). The first fraction (bp ~95°C) was collected as a clear oil (2.1 g; 12.6 mmol, 72%) and was identified as 4-dimethoxymethyltoluene (**5b**), bp 93–95°C (10 mmHg): ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.34 (s, 3H, Ar-C*H*$_3$), 3.30 (s, 6H, –OC*H*$_3$), 5.35 (s, 1H, –C*H*(OCH$_3$)$_2$, 7.13 (d, 2H, *J*=7.1 Hz, Ar-*H*), 7.37 (d, 2H, *J*=7.1 Hz, Ar-*H*) The second fraction (bp 96–103°C) contained a mixture of 1-dimethoxymethyl-4-methoxymethylbenzene (**6**, 12%) and the two isomeric 1,4-dimethoxy-1,4-dimethyl-2,5-cyclohexadienes (**7b**, **8b**, 14% combined). The yields were calculated from the integration of characteristic proton NMR peaks: ^{1}H NMR (250 MHz, $CDCl_3$): **6**, δ=3.32 (s, 6H, –OC*H*$_3$), 3.35 (s, 3H, –CH$_3$–OC*H*$_3$), 4.40 (s, 2H, –C*H*$_2$–OCH$_3$), 5.36 (s, 1H, –C*H*(OCH$_3$)$_2$, 7.17 (d, 2H, *J*=7.1 Hz, Ar-*H*), 7.37 (d, 2H, *J*=7.1 Hz, Ar-*H*). Isomeric products, **7b**, **8b**, combined: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.24 (s, 40% 3H, –C*H*$_3$), 1.32 (s, 60% 3H, –C*H*$_3$), 3.04 (s, 6H, –OC*H*$_3$), 3.17 (s, 40% 3H, –OC*H*$_3$), 3.35 (s, 60% 3H, –OC*H*$_3$), 5.77 (s, 60% 4H, –CH=C*H*–), 5.81 (s, 40% 4H, –CH=C*H*–).

2.9.2. Electrochemical oxidation of 4-methoxytoluene (1c). 4-Methoxytoluene (**1c**, 2.14 g; 17.5 mmol) was treated according to the general method. The orange residue (2.97 g) was distilled under reduced pressure. The first fraction (bp ~105°C 10 mmHg) was collected as a clear oil (2.6 g; 14.3 mmol, 81%) and was identified as 1-dimethoxymethyl-4-methoxybenzene, **5c**, bp 100–105°C (10 mmHg): ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.35 (s, 6H, –OC*H*$_3$), 3.79 (s, 3H, Ar-OC*H*$_3$), 5.34 (s, 1H, –C*H*(OCH$_3$)$_2$, 6.87 (d, 2H, *J*=6.8 Hz, Ar-*H*), 7.36 (d, 2H, *J*=6.8 Hz, Ar-*H*). The second fraction (bp 106–115°C, 10 mmHg) contained 1,1,4-trimethoxy-4-methyl-2,5-cyclohexadiene (**7c**, 6%): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.30 (s, 3H, –C*H*$_3$), 3.12 (s, 3H, –OC*H*$_3$), 3.24 (s, 3H, –OC*H*$_3$), 3.30 (s, 3H, –OC*H*$_3$), 5.90 (d, 2H, *J*=10.5 Hz, –CH=C*H*–), 6.02 (d, 2H, *J*=10.5 Hz, –CH=C*H*–).

2.10. Preparative scale electrolyses of substituted 2-methylnaphthalenes (Table 2)

These were performed at constant current and the electrolytes were either MeOH–KF (0.15 M) or CH_2Cl_2–MeOH–H_2SO_4 (80:15:1 v/v). Typical experiments are described below.

2.10.1. Electrochemical oxidation of 2-methylnaphthalene (2a). 2-Methylnaphthalene (**2a**) (1.97 g; 13.9 mmol) was electrolysed in the MeOH–KF electrolyte at a constant current of 48 mA cm^{-2} and the reaction was terminated after 5.3 F. The solution rapidly turned dark brown, and hydrogen evolution was observed at the counter electrode. The dark brown residue (1.55 g) was then dissolved in 7 ml petroleum ether (bp 40–60°C) and run through a silica gel (grade 40–60) chromatographic column with petroleum ether (bp 40–60°C) as eluent. The first fraction (R_f=0.5) was identified (by UV-HPLC) as the starting material and tars (0.13 g). The second (R_f=0.3, 0.65 g) was identified as a mixture of dimers and, by ^{1}H NMR spectroscopy of the crude fraction, a small amount of side-chain substituted product. The third fraction (R_f=0.2, 0.35 g) appeared to be a complex mixture of nuclear oxidation products and dimers.

2.10.2. The electrochemical oxidation of 2-methoxy-6-methylnaphthalene (2d). 2-Methoxy-6-methylnaphthalene (**2d**) (2.19 g, 12.7 mmol) was electrolysed in the CH_2Cl_2–MeOH–H_2SO_4 electrolyte at a constant current of 10 mA cm^{-2} and the reaction was terminated after 2.2 F. The solution rapidly turned dark brown, and hydrogen evolution was observed at the counter electrode. The dark brown residue (3.1 g) was then dissolved in 3 ml chloroform (bp 40–60°C) and run through a silica gel (grade 40–60) chromatographic column with chloroform as eluent. The first fraction (R_f=0.85) was identified (by UV-HPLC) as the starting material and tars (0.24 g). The second (R_f=0.65, 0.78 g, 72%) was identified as a the dimer (7,7′-dimethoxy-3,3′-dimethyl-1,1′-binaphthalene, **9a**) and the third (R_f=<0.4, 0.10 g) fraction as a complex mixture of nuclear oxidation products.

*7,7′-dimethoxy-3,3′-dimethyl-1,1′-binaphthalene (**9a**)*. For ring numbering see displayed structure) was obtained as colourless crystals, mp 225–227°C, Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18%; H, 6.48%. Found C, 84.10%; H, 6.52%; UV (MeCN): λ (ε, $dm^3\,mol^{-1}cm^{-1}$)=231 (68,700), 279 (10,600), 342 nm (7700). IR (KBr) (cm^{-1}): 2918, 2850, 1595, 1500, 1461, 1345, 1267, 1251, 1174, 1136, 1097, 1064, 918, 817, 804. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.44 (s, 6H, –C*H*$_3$), 3.73 (s, 6H, –OC*H*$_3$), 7.00–7.25 (m, 4H, Ar-*H*, H-2 and H-8), 7.41 (d, 2H, *J*=8.7 Hz, Ar-*H*, H-6), 7.62 (s, 2H, Ar-*H*, H-4), 7.87 (d, 2H, *J*=8.7 Hz, Ar-*H*, H-5). ^{1}H nOe enhancement experiment; irradiated δ=2.44 (–C*H*$_3$), 7.03 (3.6%, H-2), 7.62 (3.7%, H-4); ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.43, 57.11, 114.59, 125.25, 126.89, 128.63, 129.52. MS; *m/z* (%)=342.2 (M^+, 100), 296.1 (29), 171.1 (3), 156.1 (7),

147.6 (3), 126.0 (3), 91.1 (13). MS; *m/z*, M^+ 342.1619 (calcd for $C_{24}H_{22}O_2$ 342.16198).

2.10.3. Electrochemical oxidation of ethyl 6-methyl-2-naphthalene sulfonic ester (2e). Ethyl 6-methyl-2-naphthalene sulfonic ester (**13a**) (1.40 g; 5.25 mmol) was electrolysed in the CH_2Cl_2–MeOH–H_2SO_4 electrolyte at a constant current of 20 mA cm^{-2} and the reaction was terminated after 2.0 F. The solution rapidly turned dark brown, and hydrogen evolution was observed at the counter electrode. The dark brown residue (2.5 g) was then dissolved in 3 ml chloroform and run through a silica gel (grade 40–60) chromatographic column with chloroform as eluent. The first fraction (R_f=0.7) was identified (by UV-HPLC and ^{1}H NMR) as the starting material (0.74 g, 64%). The second (R_f=0.5, 0.50 g, 36%) was identified as a mixture of nuclear mono-methoxylated products, in which *ethyl 4-methoxy-6-methyl-2-naphthalene sulfonic ester* (**10**, 0.40 g, 27%) was identified. The yield was calculated by integrating characteristic ^{1}H NMR signals. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.29 (t, 3H, *J*=7.1 Hz, –CH_2–CH_3), 2.48 (s, 3H, Ar-CH_3), 3.90 (s, 3H, Ar-OCH_3), 4.16 (q, 2H, *J*=7.1 Hz, –CH_2–CH_3), 7.43 (d, 1H, *J*=8.4 Hz, Ar-*H*, H-4), 7.63 (s, 1H, Ar-*H*, H-1), 7.83–7.87 (m, 1H, Ar-*H*, H-5), 8.24 (d, 1H, *J*=8.4 Hz, Ar-*H*, H-3), 8.44 (s, 1H, Ar-*H*, H-7). The third (R_f=<0.4, 0.27 g) fraction appears to be a complex mixture of nuclear oxidation products.

2.11. Anodic oxidation of 2-CH_2Ar substituted naphthalenes (Table 4)

The electrolysis conditions are described in a footnote to Table 4. Products were typically isolated and purified by flash chromatography (silica grade 40–60) with chloroform eluent. Their characterisation is exemplified below.

2.11.1. 2-(4-Chlorobenzyl) naphthalene (2i). (0.38 g; 1.5 mmol; 0.05 M) was electrolysed to 8 F in MeOH–CH_2Cl_2 (10% v/v)–KF (0.2 M) at constant current (40 mA; 6.4 mA cm^{-2}). The crude product mixture obtained was separated and purified by flash chromatography (silica grade 40–60) using chloroform as eluent. Combining and evaporation of the appropriate fractions (R_f=0.65) gave *2-(4-chlorobenzyl)-1,4-naphthoquinone* (**13**, Z=Cl) (40 mg; 9%) as an oil which after recrystallisation from ethanol gave colourless crystals, mp 99–101°C (lit.,[36,37] 103–104°C).

The fractions (R_f=0.5), after recrystallisation from ethanol, gave *3-(4-chlorobenzyl)-4,4-dimethoxynaphthalene-1-(4H)-one* (**12**, Z=Cl) (150 mg; 30%) as opaque needles, mp 144–146°C. Anal. calcd for $C_{19}H_{17}O_3Cl$: C, 69.40%; H, 5.21%; Cl, 10.78%. Found C, 69.35%; H, 5.29%; Cl, 11.12%. IR (KBr) (cm^{-1}): 3104, 2972, 2377, 1638 (strong, broad), 1600, 1461, 1369, 1318, 1246, 1154, 1119, 1035, 892, 859, 816, 696, 655. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.93 (s, 6H, –OCH_3), 3.69 (d, 2H, *J*=1.6 Hz, =C–CH_2–Ph), 6.21 (t, 1H, *J*=1.6 Hz, –CO–C*H*=C), 7.18 (d, 2H, *J*=8.6 Hz, Ar-*H*), 7.33 (d, 2H, *J*=8.6 Hz, Ar-*H*), 7.52 (ddd, 1H, *J*=7.8, 7.0, 1.6 Hz, Ar-*H*), 7.68–7.78 (m, 2H, Ar-*H*), 8.08 (ddd, 1H, *J*=7.8, 1.6, 0.6 Hz, Ar-*H*). ^{13}C NMR (63 MHz, $CDCl_3$): δ=34.86, 51.43, 98.32, 126.22, 126.72, 128.96, 129.60, 131.28, 132.43, 132.90, 133.68, 135.30, 139.05, 158.18, 183.41. ^{1}H nOe NMR (250 MHz, $CDCl_3$): irradiation at 3.69 ppm (=C–CH_2–Ph); 2.93 (4.4%, 6H, –OCH_3), 6.21 (1H, –CO–C*H*=C), 7.18 (6.5%, 2H, Ar-*H*). MS; *m/z* (%)=328.1 (M^+, 4), 269.1 (100), 265.0 (35), 261.1 (46), 247.1 (17), 203.1 (80), 115.1 (19), 105.0 (19). MS; *m/z*, M^+ 328.0858 (calcd for $C_{19}H_{17}O_3Cl$ 328.08663).

2.11.2. 2-(α,4-Dimethoxybenzyl)-naphthalene (14, Z=OMe). Similar electrolysis of 2-(4-methoxybenzyl)-naphthalene (**2h**, 0.372 g; 1.5 mmol; 0.05 M), to 8.0 F and similar work-up gave *2-(α,4-dimethoxybenzyl)-naphthalene* (**14**, Z=OMe, 50 mg; 0.18 mmol; 12%) as an oil which could not be crystallised. Yields were calculated from the integration of characteristic ^{1}H NMR signals. ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.40 (s, 3H, –CH(OCH_3)-Ar), 3.76 (s, 3H, –Ph–OCH_3), 5.35 (s, 3H, –C*H*(OCH_3)-Ar, 6.85 (d, 2H, *J*=8.8 Hz, Ar-*H*), 7.29 (d, 2H, *J*=7.0 Hz, Ar-*H*), 7.38–7.46 (m, 3H, Ar-*H*), 7.75–7.82 (m, 4H, Ar-*H*).

2.12. Batch oxidations with DDQ[17,38,39]

General method for side-chain oxidation. To a hot (ca. 80°C), magnetically stirred solution containing acetic acid (typically 90 ml), water (typically 10 ml) and the substrate (typical conc. 0.2 M), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added in portions. The reaction mixture rapidly turned dark green (CT complexation). The mixture was then heated and allowed to reflux for 4 h, resulting in a dark red solution (2,3-dichloro-5,6-dicyano-1,4-hydroquinone formation). Standard thin layer chromatography or HPLC techniques were used to monitor the reaction. The reaction mixture was allowed to cool to room temperature, prompting a precipitation of the hydroquinone, and the solvents evaporated off using a rotary evaporator. The residue was dissolved in chloroform (typically 80 ml), filtered and poured into dilute aqueous hydrochloric acid (150 ml, 2 M). The organic phase was separated and the aqueous phase extracted with chloroform (3×40 ml). The combined organic layer was washed with dilute sodium bicarbonate (3×80 ml), water (2×60 ml) and dried ($MgSO_4$). The filtered solution was evaporated under reduced pressure to give the crude product.

These procedures are exemplified in the following descriptions of the preparation of 6-methoxy-2-naphthalene carboxaldehyde (**3d**) from different substrates and the preparation of the adduct (**15**) by oxodation with DDQ in dry benzene.

2.12.1. Oxidation of 2-methoxy-6-methylnaphthalene (2d). 2-Methoxy-6-methylnaphthalene (**2d**) (3.44 g; 0.02 mol; 0.2 M) was treated according to the general oxidation method using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (18.0 g; 0.06 mol; 3 equiv.) that was added in portions. The crude product mixture was purified by short column flash chromatography (silica grade 40–60) using chloroform as eluent. Collection of the appropriate fractions, evaporation and recrystallisation from ethanol gave **3d** (3.35 g; 0.018 mol; 90%) as off-white micro crystals, mp 79–81°C (lit.,[35] 80–81°C).

2.12.2. Synthesis of 2-methoxy-6-naphthalene carboxaldehyde (3d) using 2-hydroxymethyl-6-methoxy-naphthalene (2p). 2-Hydroxymethyl-6-methoxy-naphthalene (**2p**) (3.76 g; 0.02 mol; 0.2 M) was treated according to the general oxidation method using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (9.0 g; 0.03 mol; 1.5 equiv.) that was added in portions. The crude product mixture was purified by short column flash chromatography (silica grade 40–60) using chloroform as eluent. Collection of the appropriate fractions, evaporation and recrystallisation from ethanol gave the title compound (3.54 g; 0.019 mol; 95%) as off-white micro crystals.

2.12.3. Synthesis of 2-methoxy-6-naphthalene carboxaldehyde (3d) using 2-acetoxymethyl-6-methoxynaphthalene (2q). 2-Acetoxymethyl-6-methoxynaphthalene (**2q**) (4.60 g; 0.02 mol; 0.2 M) was treated according to the general oxidation method using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (9.0 g; 0.03 mol; 1.5 equiv.) that was added in portions. The crude product mixture was purified by short column flash chromatography (silica grade 40–60) using chloroform as eluent. Collection of the appropriate fractions, evaporation and recrystallisation from ethanol gave the title compound (3.54 g; 0.019 mol; 95%) as off-white micro crystals.

2.12.4. Synthesis of 6-methoxy-2-naphthalene-DDQ adduct (15) using 2-methoxy-6-methylnaphthalene (2d) in dry benzene. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.57 g; 2.5 mmol) was added in portions to a hot (ca. 50°C), magnetically stirred solution of 2-methoxy-6-methylnaphthalene (**2d**) (0.43 g; 2.5 mmol) in dry benzene (50 ml). The reaction mixture rapidly turned dark green (CT complexation). The mixture was heated until reflux for 8 days, gradually resulting in a pale orange colouration of the solution (2,3-dichloro-5,6-dicyano-1,4-hydroquinone formation). Small samples of the mixture were analysed by UV-HPLC to monitor the reaction. The reaction mixture was allowed to cool to room temperature, prompting a precipitation of a yellowish solid that was filtered. The solid was dried (110°C, ca. 10 mmHg) removing any volatile naphthalenes. Recrystallisation of the crude product five times from benzene gave the title compound (0.70 g; 1.75 mmol; 70%) as yellow micro crystals; mp>320°C. IR (KBr) (cm^{-1}): 3323, 3034, 1376, 1200, 1105, 1032, 892, 825, 739, 700, 658, 614. ^{1}H NMR (250 MHz, CD_3CN): δ=3.99 (s, 3H, Ar-OCH_3), 5.44 (s, 2H, Ar-CH_2–O), 7.26 (dd, 1H, J=9.0 Hz, J=2.4 Hz, Ar-H^7), 7.37 (d, 1H, J=2.4 Hz, Ar-H^5), 7.65 (dd, 1H, J=8.6, 1.7 Hz, Ar-H^3), 7.87 (d, 1H, J=9.1 Hz, Ar-H^8), 7.89 (d, 1H, J=8.7 Hz, Ar-H^4), 7.95 (s, 1H, Ar-H^1). Solid state ^{13}C NMR (75 MHz): δ=54.72, 80.95, 103.94, 108.39, 110.55, 119.60, 127.45, 134.71, 155.12, 157.49. MS; *m/z* (%)=367.0 (M^+−[CH_3O−=31], 3), 317.0 (3), 267.0 (5), 230.0 (46), 228.0 (70), 171.1 (38), 78.0 (100). MS; *m/z*, (M^+−CH_3O) 366.9681 (calcd for $C_{19}H_{10}Cl_2N_2O_2$, 367.004).

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