Unsymmetrical Anodic Coupling of Veratrole with Various Anisole Derivatives. Products and Mechanisms

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The co-electrolysis of veratrole (1) with anisole (2a), phenetole (2b), 3-methylanisole (2c), 2-methylanisole (3), 2,5-dimethylanisole (4), and 2,6-dimethylanisole (6) have been investigated in trifluoroacetic acid–dichloromethane solvent. With 2a–c good yields of “tetrameric” 5-aryl substituted triphenylene derivatives (10a, 10b or 11) were obtained, probably by initial coupling of the veratrole cation radical (1+) with the anisole derivative or its cation radical to an unsymmetrical dimer (8 or 11) followed by dimerisation and intramolecular cyclisation to the product. With 3, 4 or 5 only “trimeric” products from coupling of two veratrole units with one of the anisole units (15 or 26) or from coupling of one veratrole unit with two of the anisole units (17, 22, 25 or 27) were observed.

The oxidative coupling of benzene derivatives to biphenyls is a reaction of great synthetic value. One of the first attempts to achieve this reaction by anodic oxidation of phenol methyl ethers was made by Erdman.1 In our laboratories the anodic coupling of hydroxy 2,3 and methoxy 4–8 substituted aromatic compounds has been studied extensively. In particular, symmetrical intermolecular 4 and symmetrical as well as unsymmetrical intramolecular 5–8 anodic couplings of methoxy aromatics have been studied in detail and the synthetic utility of these reactions has been clearly demonstrated. In this study anodic oxidation has been applied to achieve unsymmetrical coupling of veratrole (1,2-dimethoxybenzene, 1) with various anisole (methoxybenzene) derivatives (2–5).

RESULTS

The products formed in the co-electrolysis experiments along with the yields are given in Table 1. The identifications of the products are based on spectroscopic data and previous findings4–8 concerning the coupling mode of methoxy aromatics. In the co-electrolysis of veratrole with anisole (2a), phenetole (ethoxybenzene, 2b), or 3-methylanisole (2c) mass spectral data and elemental analysis indicated that the major product was formed by coupling of two veratrole units with two units of the anisole derivative with formation of a total of four new carbon–carbon bonds. The structures that best fit these data as well as the NMR-spectral data (see Table 2), are 10a, 10b and 13. In the NMR spectra of the compounds corresponding to structures 10a and 10b the hydrogens on carbons 11 and 12 (designated H-11 and H-12 in the following; the numbering of the triphenylene ring system is shown in formula 7) should appear as AB quartets with a coupling constant of about 9 Hz. Hydrogens H-2', H-3', H-5', and H-6' should appear as AA'BB' quartets with coupling constants of about 9 Hz. All the other aromatic protons should appear as singlets. All these features were actually observed (Table 2). The observed differences in chemical shifts between the various aromatic and methoxyl protons are also very well explained in terms of structures 10a and 10b (in particular the low field shift of H-12 and the high field shift of the C-8 methoxy group). The total absence of spin–spin couplings in the NMR spectrum of the main product from co-electrolysis of 1 and 2c clearly shows that its structure cannot be 10c as would have been
Table 1. Products and yields from the anodic oxidation of veratrole (1) and anisole (2a), phenetole (2b), 3-methylandisole (2c), 2-methylanisole (3), 2,5-dimethylisooisole (4) or 2,6-dimethylanisole (5); of 4-methylveratrole (6) and 2a, and of 3,3',4,4'-tetramethoxybiphenyl (14) and 2a.a

<table>
<thead>
<tr>
<th>Coelectrolysis of:</th>
<th>Products containing the veratrole unit (yield based on veratrole in %b)</th>
<th>Other products isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + 2a</td>
<td>10a (60)</td>
<td>4,4'-dimethoxybiphenyl</td>
</tr>
<tr>
<td>1 + 2b</td>
<td>10b (54)</td>
<td>4,4'-diethoxybiphenyl</td>
</tr>
<tr>
<td>1 + 2c</td>
<td>13 (48)</td>
<td>4,4'-dimethoxy-2,2'-dimethylbiphenyl</td>
</tr>
<tr>
<td>1 + 3</td>
<td>15 (31); 17 (14)</td>
<td>4,4'-dimethoxy-3,3'-dimethylbiphenyl</td>
</tr>
<tr>
<td>1 + 4</td>
<td>28 (34)</td>
<td></td>
</tr>
<tr>
<td>1 + 4c</td>
<td>27 (16)</td>
<td></td>
</tr>
<tr>
<td>1 + 5</td>
<td>7 (55); 22 (2); 25 (3); 26 (36)</td>
<td>4,4'-dimethoxy-3,3',5,5'-tetramethylibiphenyl</td>
</tr>
<tr>
<td>6 + 2a</td>
<td>3,3',4,4'-tetramethoxy-6,6'dimethylbiphenyl (93)</td>
<td></td>
</tr>
<tr>
<td>14 + 2a</td>
<td>29 (90)</td>
<td></td>
</tr>
</tbody>
</table>

*aFor details see experimental section. bIn all electrolysis experiments 1, 6 or 14 were recovered in an amount which together with the amount of these compounds found in the products well accounted for all starting material. cIn this experiment, reduction with zinc dust was omitted from the work-up procedure (see Experimental).

expected. Instead, structure 13 is suggested for this product. The isomeric compound with a methoxy group at C-9 and a methyl group at C-11 fits the NMR data as well as structure 10c. However, from our previous studies4-8 we know that the position para to a methoxy group is the preferred coupling site. In fact, the ortho-para coupling observed in the coelectrolysis of 1 with 4 or 5 (in 5 the ortho position is activated by a methyl substituent) to our knowledge are the first examples of such a coupling. The very low field shift of H-12 in the NMR spectra of compounds 10a—13 and 13 indicates that the triphenylene ring system is twisted due to steric interference between the substituents. The lowest field shift for H-12 is observed in the NMR spectrum of 13 where the steric interference between the

Table 2. NMR data for the compounds 10a, 10b and 13.a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aromatic protons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-12 (C-1 C-4 C-6)c</td>
</tr>
<tr>
<td>10a</td>
<td>8.48b 7.92 7.74 7.68 7.30 — 7.34 7.35d 7.02d — — —</td>
</tr>
<tr>
<td>10b</td>
<td>8.18b 7.70 7.54 7.48 7.25 — 7.18b 7.18d 6.89d — — —</td>
</tr>
<tr>
<td>13</td>
<td>9.13   7.74 7.63 7.35 — 6.82c —</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Methoxyl substituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C-2) (C-3) (C-7) (C-3’))c</td>
</tr>
<tr>
<td>10a</td>
</tr>
<tr>
<td>10b</td>
</tr>
<tr>
<td>13</td>
</tr>
</tbody>
</table>

*aUnless otherwise stated the shifts refer to singlet absorption peaks. bDoublet, J = 9 Hz. cThe actual order of assignment of these shifts has not been established. dTwo proton doublet, J = 8 Hz. eThese assignments could be reversed.

C-8 and the C-9 substituents would be very great in a planar configuration.

Mass spectral and analytical data indicate that one of the two main products from the coelectrolysis of veratrole and 2-methylanisole (3) is formed by coupling of two units of I and one unit of 3 through three new carbon—carbon bonds, whereas the other is formed by coupling of one unit of I with two units of 3 also through three new carbon—carbon bonds. On the basis of NMR data the former product is assigned structure 15. For the latter product both structure 17 and the isomeric 2,7,10,11-tetramethoxy-3,6-dimethyltriphenylene fit the analytical and spectroscopic data. However, no coupling between I and 4,4'-dimethoxy-3,3'-dimethylbiphenyl occurs in the coelectrolysis of these two compounds we can exclude the second possibility.

Two different products could be obtained in high yield from the coelectrolysis of veratrole and 2,5-dimethylanisole (4) depending on whether reduction with zinc dust was used in the work-up or not. Mass spectral data (molecular weight change of plus two mass units) indicated that zinc dust (in combination with TFA) affected hydrogenation of a double bond in the primary electrolysis product. NMR and mass spectral data indicated that the primary product was formed by coupling of one unit of veratrole with two units of 4 through three new carbon—carbon bonds and with, simultaneously, loss of one methyl group from one of the methoxy substituents. Furthermore, the NMR shifts of the methyl groups attached to a carbon atom (C-methyl groups) showed that the aromaticity of one of the coupled rings had been lost, and the IR spectrum showed that the coupling product contained a carbonyl function. On the basis of this evidence structure 27 was ascribed to the primary electrolysis product. The compound obtained by reduction with zinc dust was assigned structure 28 as one of the C-methyl groups of the dienone ring gave rise to a doublet (J = 6.48 Hz) at 1.45 ppm in the NMR spectrum. This would not have been the case if the other double bond in the dienone ring of 27 had been reduced. The hydrogenation with zinc dust was not stereospecific. The isomer with the two methyl groups of the cyclohexenone ring in the cis-configuration (arising from addition of hydrogen from the less hindered side of the dienone ring of 27) as well as the isomer with these two methyl groups in the trans configuration are formed. The ratio between the two isomers was found to be 8:1. Since addition of hydrogen from the less hindered side should be favoured the cis-isomer is probably the dominating product. Three different coupling products were obtained from the coelectrolysis of veratrole and 2,6-dimethylanisol (5) which were assigned structures 22, 25 and 26 on the basis of analytical and spectral data. In particular, it should be noted that all the aromatic protons in both compounds 22 and 26 have different NMR shifts and that no proton—proton spin couplings between them are observed. This excludes all structures with a symmetry plane.

The coupling product from coelectrolysis of anisole and 3,3',4,4'-tetramethoxybiphenyl (14) must be 29. Elemental analysis and the mass spectrum show that only one anisole unit couples with 14 and that two new carbon—carbon bonds are formed. Two structures are possible, 29 and 2,3,7,9,10-pentamethoxytriphenylene. However, the NMR spectrum of the product contains a two-proton AB quartet (J = 9 Hz) and four one proton singlets which is only compatible with structure 29.

DISCUSSION

The formation of all the products observed in the coelectrolysis experiments can be rationalised in terms of coupling between veratrole (I) or its cation radical (I⁺), the anisole derivative (An) or the cation radical thereof (An⁺), the cation radical of the veratrole dimer (I₂⁺), and the cation radical (I — An⁺) of the coupling product of veratrole and the anisole derivative, followed by intramolecular oxidative cyclosisations, in certain cases rearrangement, and deprotonations to give the final products. Each coupling step can involve either two cation radicals or a cation radical and neutral substrate.

The product studies do not allow us to distinguish between the two coupling reactions. Furthermore, the various cation radicals can be formed both by heterogeneous electron transfer at the anode and by homogeneous electron transfer in the solution from neutral molecules to a cation radical. The possible reaction pathways leading to the observed products are summarised in Scheme 1 and illustrated in more detail in Schemes 2—4.

Depending on the products formed the results of the coelectrolysis experiments can be divided into three groups:

Group one. In this group only tetramers of structure 10 or 13 are observed (coelectrolysis of I with 2a, 2b or 2c). Veratrole is 0.3—0.4 V more easily
Scheme 1. Summary of possible primary reactions for formation of the products observed in the coelectrolysis experiments. 1 is veratrole and $I^+$ is the cation radical of veratrol. An is the anisol derivative and $An^+$ its cation radical. $I_2^+$ is the cation radical of the veratrol dimer ($I_2 = I_2^+$), $I-An^+$ is the cation radical of the coupling product between 1 and An, etc. One arrow corresponds to a simple electron transfer reaction. Two arrows indicate a multistep reaction involving deprotonations, further electron transfers and formation of carbon–carbon bonds (both inter- and intramolecular bonds). The intermediates $I_2$, $I-An$, $I_2-An$ and $I_2-An_2$ are shown in their cation radical form as they are all considerably more easily oxidised than either 1 or An.

oxidized than are any of the three anisole derivatives $2a-c$. That is, veratrole can be selectively oxidized to its cation radical ($I^+$) in these coelectrolyses. $I^+$ then reacts with $2a$, $2b$ or $2c$ to give an unsymmetrical dimer (8 or 9 in Scheme 2; eqns. 1, 2 and 5 in Scheme 1). The absence of 7 or trimers containing two veratrol units (like 13) clearly indicates that $I^+$ does not dimerise or attack 1 electrophilically under these circumstances. Surprisingly, coelectrolysis of 1 and 2c does not give the expected tetramer 10c where the initial bond formation between 1 and 2c (eqn. 5 in Scheme 1) has occurred between positions para to methoxy groups. (Instead the dimer 11 where the new bond is to the position meta to the methoxy group of 2c is formed.) However, we believe that the initial attack of $I^+$ is on the 4-position of 2c and that the resulting cation radical rearranges faster than it undergoes deprotonation due to the steric interference of the methyl group. Normally deprotonation is a much faster reaction. The final product 13 is formed by dimerisation of 11 to 12 followed by intramolecular cyclisation. Similarly, we believe that 10a and 10b are formed via dimerisation of the unsymmetrical biphenyls 8a and 8b. As shown in Scheme 1 (eqns. 11 and 12) the tetramers 10 and 13 could also be formed by a stepwise coupling of veratrole and anisole units. However, we can exclude these mechanisms since coelectrolysis of 14 and anisole yields only the primer 29, and since the results of the coelectrolysis of 1 with 3, 4 or 5 clearly indicate that the favoured reaction of a $I-An_2$ intermediate is intramolecular cyclisation. No evidence of a reaction such as 12 (Scheme 1) was in fact obtained, although it is evident from the products that intermediates like $I-An_2$ do occur in the coelectrolyses. It is noteworthy that only one of the two possible intramolecular cyclisation reactions of the intermediates 9 and 12 actually occur. The second intramolecular cyclisation would have resulted in a dibenzo[d,f,g,op]naphthalene derivative. At least compound 13 with an unsubstituted position para to a methoxy group in the 5-arylsubstituent should be able to undergo the second cyclisation. The reason for this is probably steric interference between the substituents which would impose a twisted configuration on the dibenzo-
Scheme 3. Coelec trolysis of veratrole (I) and 2- methyl anisole (3). Possible mechanisms for the formation of the products. The underlined structures correspond to products actually isolated. The numbers in parentheses refer to the corresponding reactions in Scheme 1.

oxidation of I to $I^{+}$ is not expected in these coelectrolyses. Instead, the cation radicals of both starting materials are probably formed simultaneously at the electrode and by charge transfer in electron exchange equilibria in the solution. Still, the product studies clearly indicate (products 17, 22, 25 and 27) that unsymmetrical biphenyls (16 or 18 in Schemes 3 and 4) are intermediates in these coelectrolyses as well. However, in no case was dimerisation of these biphenyl derivatives observed. Only products formed by coupling of three units of starting materials were observed. Possible mechanisms for the formation of the two coupling products, 15 and 17, isolated from the coelectrolysis of 1 and 3 are shown in Scheme 3 and involve combinations of reactions 1–3 and 5–9 in Scheme 1. The product 17 can only be formed by coupling of 16 or 16' with 3 or 3' (reactions 5 and 9 in Scheme 1), whereas the other product, 15, can arise both from 16/16' by coupling with 1/I+/ (reactions 5 and 8 in Scheme 1) or from 14/14' by coupling with 3/3' (reactions 3 and 7 in Scheme 1).

In the coelectrolysis of veratrole and 4 only one coupling product containing the veratrole unit was observed (27 or its hydrogenation product 28). 27 most likely is formed by the same mechanism as 25 (cheme 4). It should be noted that the sole

reaction of the veratrole cation radical in this case is coupling with 4/4+ in the unsubstituted 4-position to form 3,4,4'-trimethoxy-2,5'-dimethylbiphenyl (or the cation radical thereof). This species couples further with 4/4+, now in the methyl substituted 2-position to give — after further oxidation, cyclisation, and demethylation — the final product 27.

**Group three.** In this group both trimers of the kind observed in group two and hexamethoxytriphenylene (7) are observed; coelectrolysis of veratrole and 5. As in group two, no selective oxidation of 1 is expected to occur. In fact, this coelectrolysis is the least selective of them all and four coupling products containing the veratrole unit, 7, 22, 25 and 26 were isolated. Possible mechanisms for their formation are shown in Scheme 4. It should be noted that 55% of the veratrole is oxidised to 7 which was not observed in any of the other coelectrolyses.

The coelectrolysis of 4-methylveratrole (6) and anisole (see Table 1) gave no unsymmetrical coupling product. Only the dimer of 6 (3,3',4,4'-tetramethoxy-2,2'-dimethylbiphenyl) was isolated. Apparently, introduction of a 4-substituent in veratrole (as in the intermediates 8 and 9 in Scheme 2) makes the dimerisation reaction very favourable.

**CONCLUSIONS**

The mechanistic hypothesis that we have made (Schemes 1—4) are only meant to signify possible routes by which the observed products may be formed. The differences in oxidation potentials of
all the substrates are not so great that any of the
possible electron transfer reactions (a) can be
excluded. Therefore, all reaction pathways could
be controlled by the relative rate constants together
\[
\text{Ar}_1^+ + \text{Ar}_2 \xrightleftharpoons{K_{\text{exchange}}} \text{Ar}_1 + \text{Ar}_2^+ \quad (a)
\]
with the pertinent concentrations of intermediates and
no simple relationship seems to exist between
relative oxidation potentials and nucleophilicities
of the starting materials and the products obtained.
However, it is clear from the product studies that
a degree of selectivity is observed and that the
mixed coupling provide a useful route to the com-
 pound which cannot be obtained by more con-
ventional synthetic procedures.

**EXPERIMENTAL**

General procedures and apparatus used for vol-
tammetry and coulometry and the purification of
solvents were conventional and have been described
in previous papers.2–8 The NMR spectra were
recorded in deuterochloroform with Me$_4$Si as
internal reference. IR spectra were recorded in KBr
tables. The starting materials (1–5) were
commercial products purified further by distillation.

**Preparative electrolyses. General.** The veratrole
derivative (1 or 6, 20 mmol) and phenethol (1b) or
the anisole derivative (1a, 1c, 3, 4 or 5), 60 mmol,
were dissolved in TFA—DCM (1:3, 200 ml) con-
taining n-Bu$_4$NBF$_4$ (4 g) and transferred to the
anode chamber of a closed two-compartment elec-
trolysis cell divided by a glass frit (G-4).
Catholyte was pure TFA (50 ml) containing
n-Bu$_4$NBF$_4$ (1 g). The anode was a platinum cylinder
(150 cm$^2$) and the cathode a coil of platinum wire.
The electrolyses were carried out at constant current
(500 mA) with efficient magnetic stirring. The
temperature was kept at 12°C by external cooling and
nitrogen was bubbled through the solution during
the entire electrolysis. When 6300 Coulomb (cor-
responding to 3 F per mol of the veratrole derivative)
of current had been passed through the cell, zinc
dust (9 g) was added and the stirring was continued
until the emerald green cation radical colour of the
electrolysis mixture had disappeared. Water (150
ml) was added and the organic phase was separated
and washed with water (150 ml), saturated bicar-
obonate solution (2×100 ml), and water (150 ml),
and then evaporated to dryness. The residue was
dissolved in methanol (75 ml) and left at 0°C for 24
h. If any precipitate had formed it was collected by
filtration and analysed. The filtrate was evaporated
to dryness and the residue was chromatographed
on silica gel (Merck 60, 200 g) with a toluene-
diethyl ether gradient. The various fractions were
analysed by TLC, NMR and mass spectroscopy.
The results are summarised in Table 1.

**Coelectrolysis of veratrole (1) and anisole (2a).** Treatment of the crude electrolysis product with
methanol gave yellow crystals (2.90 g) which were
recrystallised from DMC-methanol (3:1) to give
greyish crystals (2.70 g, m.p. 201–203°C; identified
as 2,3,7,8,10-pentamethoxy-5-(4-methoxyphenyl)-
triphenylene (10a) by their NMR (Table 2) (360
MHz) δ 8.48 (1H,d(J = 9Hz), 7.92 (1H,s), 7.74 (1H,s)
7.68 (1H,s), 7.35 (2H,d(J = 8Hz)), 7.34 (1H,d(J = 9Hz)),
7.30 (1H,s), 7.02 (2H,d(J = 8Hz)), 4.13 (3H,s), 4.12
(3H,s), 4.06 (3H,s), 3.84 (3H,s), and 3.31 (3H,s) ppm.
Anal. calc. for C$_{30}$H$_{28}$O$_6$: C 74.4, H 5.8. Found:
C 74.3, H 5.8. M$^+$ 484 m/e.

Chromatography of the methanol soluble part of
the electrolysis product gave starting materials,
4,4′-dimethoxybiphenyl, and a trace of 10a.

**Coelectrolysis of veratrole and phenethol (2b).** Treatment of the crude electrolysis product with
methanol gave brownish crystals (1.07 g) which were
recrystallised from chloroform—ethanol (3:2) to
give greyish crystals m.p. 168–170°C, identified as
10-ethoxy-5-(4-ethoxyphenyl)-2,3,7,8-tetramethoxy-
triphenylene (10b) by their M$^+$ 512 m/e; NMR
(360 MHz) δ 8.18 (1H,d(J = 9Hz), 7.70 (1H,s), 7.54
(1H,s), 7.48 (1H,s), 7.25 (1H,s), 7.18 (2H, d(J = 8Hz)),
7.04 (2H,d(J = 9Hz)), 6.89 (2H,d(J = 8Hz)), 4.12
(3H,s), 4.11 (3H,s), 4.04 (3H,s), 3.95 (2H,q), 3.29
(3H,s), 1.43 (3H,t), and 1.23 (3H,t) ppm; anal. calc.
for C$_{32}$H$_{32}$O$_6$: C 75.0, H 6.3. Found: C 75.2, H 6.3.
Chromatography of the methanol soluble part of
the electrolysis product gave starting materials,
4,4′-diethoxybiphenyl (1.62g), and 10b (1.70g).

**Coelectrolysis of veratrole and 3-methyl-anisole (2c).** No precipitate was obtained on treatment of
the crude electrolysis product with methanol. Chrom-
atography gave starting materials, 4,4′-dimethoxy-
2,2′-dimethylbiphenyl, and 5-(3-methoxy-5-methyl-
phenyl)-2,3,7,8,9-pentamethoxy-11-methyltriphen-
ylene (13), 2.50 g, m.p. 108–110°C (ethanol-
toluene = 2:1), identified by its M$^+$ 512 m/e; NMR δ
(360 MHz) 9.13 (1H,s), 7.74 (1H,s), 7.63 (1H,s),
7.35 (1H,s), 7.02 (1H,s), 6.82 (1H,s), 6.71 (2H,s), 4.07
(3H,s), 4.04 (6H,s), 4.00 (3H,s), 3.74 (3H,s), 3.31
(3H,s), 2.36 (3H,s), and 2.17 (3H,s) ppm; anal. calc.
for: C$_{32}$H$_{32}$O$_6$: C 75.0, H 6.3. Found: C 75.2, H 6.2.

**Coelectrolysis of veratrole and 2-methylanisole (3).** Treatment of the crude electrolysis product with
methanol gave crystals. 2.86 g, which TLC indicated
to consist of two different compounds. By prepara-
tive TLC these two compounds were isolated in
pure form and identified as 3,6,10,11-tetramethoxy-
2,7-dimethyltriphenylene (17), m.p. 260–262°C by
M$^+$ 376 m/e; NMR (360 MHz) δ 7.70 (2H,s), 7.34

(2H, s), 7.25 (2H, s), 3.93 (6H, s), 3.81 (6H, s), and 2.33 (6H, s) ppm; and 2.36, 7,10-pentamethoxy-11-methyltriphenylene (15, m.p. 240−243°C by the M* 392 m/e; NMR (360 MHz) δ 7.65 (2H, s), 7.29 (2H, s), 7.21 (2H, s), 3.93 (6H, s), 3.81 (3H, s), 3.80 (6H, s), and 2.33 (3H, s) ppm. The molar ratio between 15 and 17 was 1:3 (NMR). Chromatography of the methanol soluble part of the electrolysis product gave starting materials and 4,4'-dimethoxy-3,3'-dimethylbibiphenyl, 0.21 g.

**Coelectrolysis of veratrole and 2,5-dimethylanisole (4).** Treatment of the crude electrolysis product with methanol gave yellow crystals, 2.30 g, m.p. (ethanol−toluene = 1:2) 306−208°C, identified as a 1:4 mixture of the two isomeric (cis and trans methyl groups in the hydrogenated diene ring) dihydro compounds 28 by their M* 392 m/e; NMR (360 MHz) δ (cis isomer) 7.420 (1H, s), 6.947 (1H, s), 6.682 (1H, s) 6.226 (1H, s), 3.985 (3H, s), 3.898 (3H, s), 3.856 (3H, s), 3.0 (2H, m), 2.790 (3H, s), 1.7 (1H, m), 1.432 (3H, s), and doublet (J = 6.48 Hz) 1.154 and 1.136 ppm; and (trans isomer) δ 7.352 (1H, s), 6.947 (1H, s), 6.716 (1H, s), 3.623 (1H, s), 3.985 (3H, s), 3.898 (3H, s), 3.856 (3H, s), 3.0 (2H, m), 2.709 (3H, s), 2.296 (3H, s) 1.71 (1H, m), 1.473 (3H, s), and doublet (J = 6.48 Hz) 1.173 and 1.155 ppm; IR ν 1675 cm⁻¹ (carbonyl); anal. calc. for C₇₂H₇₅O₄: C 76.5, H 7.1. Found: C 76.6, H 7.1. Chromatography of the methanol soluble part of the electrolysis product gave starting materials and 28, 0.65 g.

When the zinc dust reduction at the end of the electrolysis was omitted, treatment of the crude product with methanol gave yellow crystals, 0.40 g, m.p. (EtOH) 138−140°C, identified as the diene one 27 by M* 390 m/e; NMR (60 MHz) δ 7.37 (1H, s), 6.70 (1H, s), 6.52 (1H, s), 6.50 (1H, s), 6.27 (1H, s), 3.98 (3H, s), 2.72 (3H, s), 1.93 (3H, s), and 1.35 (3H, s) ppm; IR ν 1670 cm⁻¹ (carbonyl); anal. calc. for C₇₂H₇₄O₄: C 76.9, H 6.7. Found: C 76.6, H 6.5. Chromatography of the methanol soluble part of the electrolysis product gave a further 0.85 g of 27.

**Coelectrolysis of veratrole and 2,6-dimethylanisole (5).** Treatment of the crude electrolysis product with methanol gave greyish crystals, 1.50 g, identified as 7 by comparison with an authentic sample. Chromatography of the methanol soluble part gave starting materials; 4,4'-dimethoxy-3,3',5,5'-tetramethylbibiphenyl, 0.59 g; 2,3,6,10-tetramethoxy-5,7,9,11-tetramethyltriphenylene (22), 0.16 g, m.p. 158−160°C, identified by its M* 404 m/e, NMR (60 MHz) δ 8.15 (1H, s), 8.00 (1H, s), 7.87 (1H, s), 7.78 (1H, s), 4.03 (3H, s), 3.59 (3H, s), 3.85 (6H, s), 2.88 (3H, s), 2.85 (3H, s), and 2.48 (6H, s) ppm, and anal. calc. for C₇₂H₇₄O₄: C 77.2, H 6.9. Found: C 77.5, H 6.8; the diene one 25, 0.20 g, m.p. 151−153°C, identified by its M* 390 m/e, NMR (60 MHz) δ 7.38 (1H, s), 6.73 (1H, s), 6.53 (1H, s), 6.48 (1H, d, J = 2 Hz), 6.27 (1H, d, J = 2 Hz), 3.98 (3H, s), 3.83 (6H, s), 1.95 (6H, s), and 1.35 (3H, s) ppm, IR ν 1670 cm⁻¹ (carbonyl), and anal. calc. for C₇₂H₇₅O₄: C 76.9, H 6.7. Found: C 76.7, H 6.8; and finally 2,3,6,7,10-pentamethoxy-9,11-dimethyltriphenylene (26), 1.46 g, m.p. 180−182°C, identified by its M* 406 m/e, NMR (60 MHz) δ 7.66 (2H, s), 7.83 (1H, s), 7.63 (1H, s), 7.50 (1H, s), 7.45 (1H, s), 4.03 (2H, s), 3.82 (3H, s), 2.83 (3H, s), and 2.47 (3H, s) ppm, and anal. calc. for C₇₂H₇₅O₄: C 73.9, H 6.4. Found: C 74.0, H 6.3. If the electrolysis was carried out in pure TFA no diene (25) could be isolated. However, a higher yield (0.45 g) of 22 was obtained.

**Coelectrolysis of 4-methylveratrole (6) and anisole.** No precipitate was formed on treatment of the crude electrolysis product with methanol. Chromatography gave apart from starting materials 3,3',4,4'-tetramethoxy-6,6'-dimethylbibiphenyl as the only product.

**Coelectrolysis of 3,3',4,4'-tetramethoxybibiphenyl (14) and anisole.** 14, 10 mmol, and anisole, 60 mmol, were coelectrolysed according to the general procedure above. However, only 4200 Coulomb of current corresponding to 2 F/mol of 14 was passed through the cell. Treatment of the electrolysis product with methanol gave yellow crystals, 3.40 g, m.p. (EtOH−CHCl₃ = 2:1) 185−187°C, identified as 2,3,6,7,10-pentamethoxytriphenylene (29) by its M* 378 m/e; NMR (360 MHz) δ 8.010 (H-12, d, J = 9.17 Hz), 7.982 (H-9, d, J = 2.45 Hz), 7.460, 7.332, 7.150, 7.143 (one proton singlets assigned to H-1, H-4, H-5, and H-8; the actual order of the assignment was not determined), 7.191 (H-11, quartet (J₁₋₂ = 9.17 Hz, J₁₋₉ = 2.45 Hz)), 3.958 (3H, s), 3.924 (3H, s), 3.921 (6H, s), and 3.907 (3H, s) ppm. Anal. calc. for C₇₂H₇₅O₄: 84.1, H 5.8. Found: C 84.2, H 5.8. Chromatography of the methanol soluble part gave starting materials and a small amount of 4,4'-dimethoxybibiphenyl (0.20 g).

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**REFERENCES**


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