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

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The coelectrolysis 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 veratrol cation radical ($1^{\cdot+}$) 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 Erdtman.[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 coelectrolysis experiments along with the yields are given in Table 1. The identifications of the products are based on spectroscopic data and previous findings[4–8] concerning the coupling mode of methoxy aromatics. In the coelectrolysis 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 coelectrolysis of *1* and *2c* clearly shows that its structure cannot be *10c* as would have been

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Table 1. Products and yields from the anodic oxidation of veratrole (*1*) and anisole (*2a*), phenetole (*2b*), 3-methylanisole (*2c*), 2-methylanisole (*3*), 2,5-dimethylanisole (*4*) or 2,6-dimethylanisole (*5*); of 4-methylveratrole (*6*) and *2a*, and of 3,3′,4,4′-tetramethoxybiphenyl (*14*) and *2a*.[a]

Coelectrolysis of:	Products containing the veratrole unit (yield based on veratrole in %[b])	Other products isolated
1+2a	*10a* (60)	4,4′-dimethoxybiphenyl
1+2b	*10b* (54)	4,4′-diethoxybiphenyl
1+2c	*13* (48)	4,4′-dimethoxy-2,2′-dimethylbiphenyl
1+3	*15* (31); *17* (14)	4,4′-dimethoxy-3,3′-dimethylbiphenyl
1+4	*28* (34)	
1+4[c]	*27* (16)	
1+5	*7* (55); *22* (2); *25* (3); *26* (36)	4,4′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl
6+2a	3,3′4,4′-tetramethoxy-6,6′dimethylbiphenyl (93)	
14+2a	*29* (90)	

[a] For details see experimental section. [b] In 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. [c] In 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 studies[4–8] 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–b* 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]

Compound Chemical shift (ppm)

Aromatic protons

	C-12	(C-1	C-4	C-6)[c]	C-9	C-10	C-11	C-2′ C-6′	C-3′ C-5′	(C-2′	C-4′	C-6′
10a	8.48[b]	7.92	7.74	7.68	7.30	–	7.34	7.35[d]	7.02[d]	–	–	–
10b	8.18[b]	7.70	7.54	7.48	7.25	–	7.18[b]	7.18[d]	6.89[d]	–	–	–
13	9.13	7.74	7.63	7.35	–	6.82[e]	–			7.02[e]	6.71	(2H)

Methoxyl substituent

	(C-2	C-3	C-7	(C-3′))[c]	C-10	C-4′	C-11	C-8
10a	4.13	4.12	4.06		3.86[e]	3.84[e]	–	3.31
10b	4.12	4.11	4.04		–[f]	–[f]	–	3.29
13	4.07	4.04(6H)		4.00	–	–	3.74	3.31

[a] Unless otherwise stated the shifts refer to singlet absorption peaks. [b] Doublet, $J=9$ Hz. [c] The actual order of assignment of these shifts has not been established. [d] Two proton doublet, $J=8$ Hz. [e] These assignments could be reversed. [f] Ethoxy groups at these carbons in *10b*.

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 *1* and one unit of *3* through three new carbon – carbon bonds, whereas the other is formed by coupling of one unit of *1* 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, as no coupling between *1* 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.

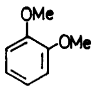
The coupling product from coelectrolysis of anisole and 3,3′,4,4′-tetramethoxybiphenyl (*14*) must be *29*. Elemental analysis and the mass spectrum show that only one anisole unit couples with *14* and that two new carbon – carbon bonds are formed. Two structures are possible, *29* and 2,3,7,9,10-pentamethoxytriphenylene. 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 (*1*) or its cation radical ($1^{\cdot +}$), the anisole derivative (*An*) or the cation radical thereof ($An^{\cdot +}$), the cation radical of the veratrole dimer ($1_2^{\cdot +}$), and the cation radical ($1 - An^{\cdot +}$) of the coupling product of veratrole and the anisole derivative, followed by intramolecular oxidative cyclisations, 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 *1* with *2a*, *2b* or *2c*). Veratrole is 0.3 – 0.4 V more easily



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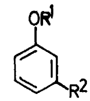
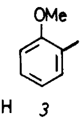


2a: R^1=Me, R^2=H
b: R^1=Et, R^2=H
c: R^1=Me, R^2=Me



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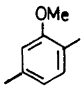

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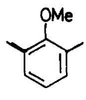

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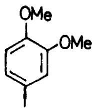

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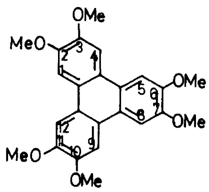

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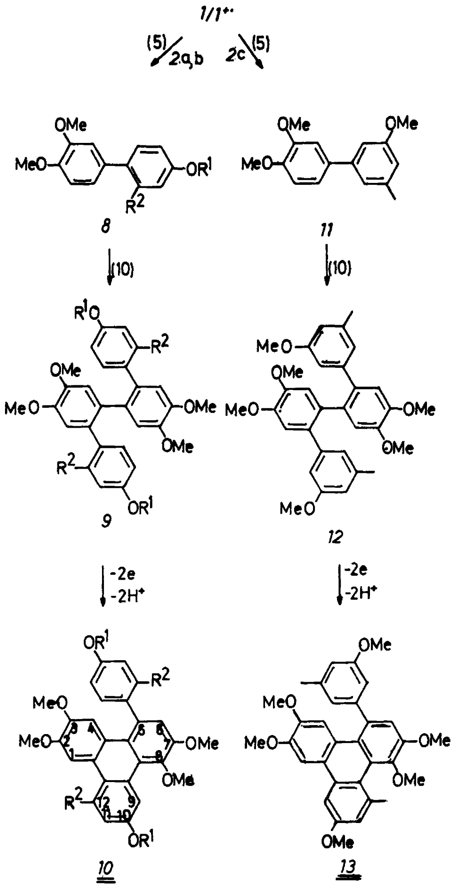
$$\begin{array}{llll}
1.\ 1-\mathrm{e} & \rightarrow & 1^{\cdot+} & \\
2.\ An-\mathrm{e} & \rightarrow & An^{\cdot+} & \\
3.\ 2\,1/1^{\cdot+} & \rightarrow\rightarrow & 1_2^{\cdot+} & \\
4.\ 1_2^{\cdot+}+1/1^{\cdot+} & \rightarrow\rightarrow & 1_3^{\cdot+} & \rightarrow\rightarrow\ 7\ \text{(trimer)} \\
5.\ 1/1^{\cdot+}+An/An^{\cdot+} & \rightarrow\rightarrow & 1\text{-}An^{\cdot+} & \\
6.\ 2An/An^{\cdot+} & \rightarrow\rightarrow & An_2^{\cdot+} & \rightarrow\rightarrow\ An_2\ \text{(biphenyl derivatives)} \\
\left.\begin{array}{l} 7.\ 1_2^{\cdot+}+An/An^{\cdot+} \\ 8.\ 1\text{-}\mathrm{An}^{\cdot+}+1/1^{\cdot+} \end{array}\right\} & \rightarrow\rightarrow & 1_2\text{-}\mathrm{An}^{\cdot+} & \rightarrow\rightarrow\ 15, 26\ \text{(trimers)} \\
9.\ 1\text{-}\mathrm{An}^{\cdot+}+An/An^{\cdot+} & \rightarrow\rightarrow & 1\text{-}\mathrm{An}_2^{\cdot+} & \rightarrow\rightarrow\ 17, 22, 25\ \text{(trimers)} \\
\left.\begin{array}{l} 10.\ 2\,1\text{-}An^{\cdot+} \\ 11.\ 1_2\text{-}An^{\cdot+}+An/An^{\cdot+} \\ 12.\ 1\text{-}An_2^{\cdot+}+1/1^{\cdot+} \end{array}\right\} & \rightarrow\rightarrow & 1_2\text{-}An_2^{\cdot+} & \rightarrow\rightarrow\ 10, 13\ \text{(tetramers)}
\end{array}$$

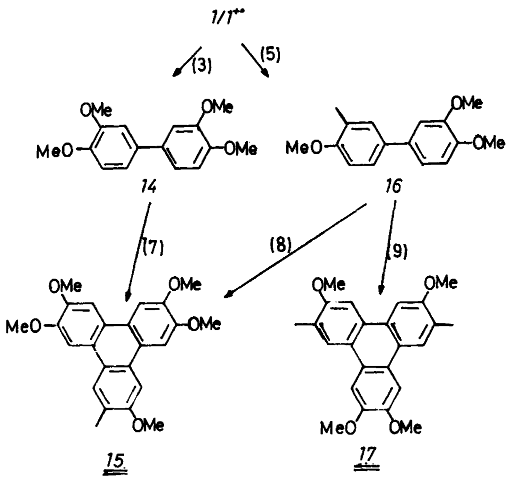
Scheme 1. Summary of possible primary reactions for formation of the products observed in the coelectrolysis experiments. *1* is veratrole and $1^{\cdot+}$ is the cation radical of veratrol. *An* is the anisol derivative and $An^{\cdot+}$ its cation radical. $1_2^{\cdot+}$ is the cation radical of the veratrol dimer ($14 = 1_2$), 1-An$^{\cdot+}$ 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 1_2, *1-An*, 1_2-*An* and 1_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 derivaties *2a–c*.[9] That is, veratrole can be selectively oxidized to its cation radical ($1^{\cdot+}$) in these coelectrolyses. $1^{\cdot+}$ 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 *15*) clearly indicates that $1^{\cdot+}$ 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 $1^{\cdot+}$ 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. Similarily, 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 trimer *29*, and since the results of the coelectrolysis of *1* with *3*, *4* or *5* clearly indicate that the favoured reaction of a $1\text{-}An_2$ intermediate is intramolecular cyclisation. No evidence of a reaction such as 12 (Scheme 1) was in fast obtained, although it is evident from the products that intermediates like $1\text{-}An_2$ 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[*fg,op*]naphthacene 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 2. a, $R^1 = Me$, $R^2 = H$; b, $R^1 = Et$, $R^2 = H$; c, $R^1 = R^2 = Me$. Coelectrolyses of veratrole (*1*) with anisole (*2a*, $R^1 = Me$; $R^2 = H$), or phenetole (*2b*, $R^1 = Et$; $R^2 = H$), or 3-methylanisole (*2c*, $R^1 = R^2 =$ Me). Possible mechanisms for the formation of the products. The underlined structures correspond to the compounds actually isolated. The numbers in parentheses refer to the corresponding reaction types in Scheme 1.

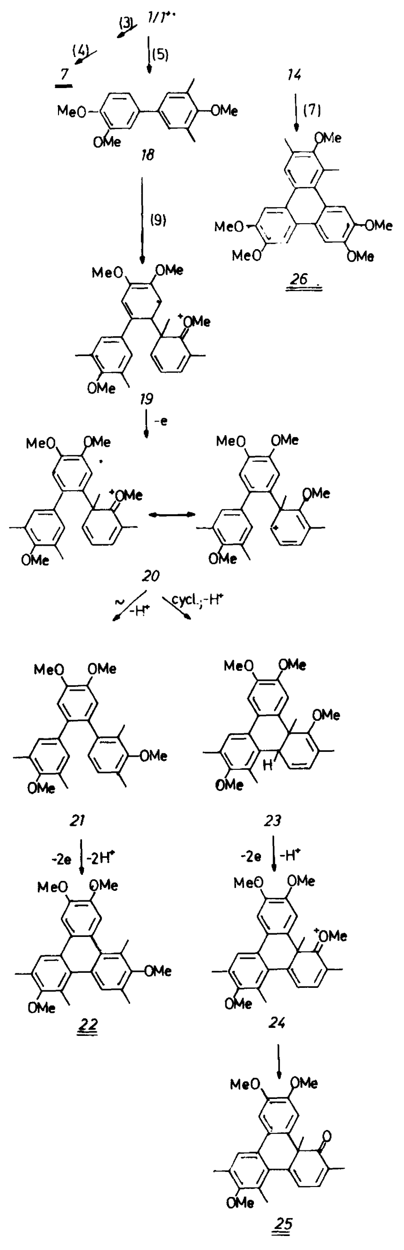
[*fg,op*]naphthacene derivative. This diminishes the conjugation between the rings and thereby the aromatic stabilisation energy. Hence, the cation radicals of *10* and *13* are more stable in the "open" than in the cyclised form (in the latter, bonding between C-4 and C-2′ has occurred).



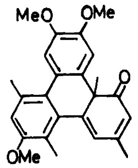
Scheme 3. Coelectrolysis of veratrole (*1*) and 2-methylanisole (*3*). Possible mechanisms for the formation of the products. The underlined structures correspond to products actually isolated. The numbers in parentheses refer to the corresponding reactions in Scheme 1.

Group two. In this group only trimers of structures *15*, *17* and/or *27* are observed. Coelectrolysis of *1* with *3* or *4*. The oxidation potentials of veratrole and *3* and *4* are quite similar.[9] Therefore, selective oxidation of *1* to $1^{\cdot +}$ 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 coelectrolysis 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 $16^{\cdot +}$ with *3* or $3^{\cdot +}$ (reactions 5 and 9 in Scheme 1), whereas the other product, *15*, can arise both from $16/16^{\cdot +}$ by coupling with $1/1^{\cdot +}$ (reactions 5 and 8 in Scheme 1) or from $14/14^{\cdot +}$ by coupling with $3/3^{\cdot +}$ (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



Scheme 4. Coelectrolysis of veratrole (*1*) and 2,6-dimethylanisole (*5*). 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.



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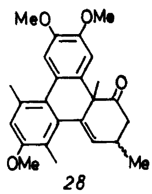

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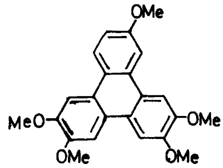

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reaction of the veratrole cation radical in this case is coupling with $4/4^{\cdot+}$ in the unsubstituted 4-position to form 3,4,4′-trimethoxy-2′,5′-dimethylbiphenyl (or the cation radical thereof). This species couples further with $4/4^{\cdot+}$, 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

$$Ar_1^{\cdot +} + Ar_2 \xrightleftharpoons{K_{\text{exchange}}} Ar_1 + Ar_2^{\cdot +} \qquad (a)$$

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 compound which cannot be obtained by more conventional synthetic procedures.

EXPERIMENTAL

General procedures and apparatus used for voltammetry and coulometry and the purification of solvents were conventional and have been described in previous papers.[2-8] The NMR spectra were recorded in deuteriochloroform with Me_4Si as internal reference. IR spectra were recorded in KBr tablets. 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) containing n-Bu_4NBF_4 (4 g) and transferred to the anode chamber of a closed two-compartment electrolysis cell divided by a glass frit (G-4). The catholyte was pure TFA (50 ml) containing $n$$Bu_4NBF_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 (corresponding 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 bicarbonate 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 phenetole (*2b*).* Treatment of the crude electrolysis product with methanol gave brownish crystals (1.07g) 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-methylanisole (*2c*).* No precipitate was obtained on treatment of the crude electrolysis product with methanol. Chromatography gave starting materials, 4,4′-dimethoxy-2,2′-dimethylbiphenyl, and 5-(3-methoxy-5-methylphenyl)-2,3,7,8,9-pentamethoxy-11-methyltriphenylene (*13*), 2.50g, 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 preparative 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 2,3,6,7,10-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′-dimethylbiphenyl, 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 dienone 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), 2.709 (3H,s), 2.200 (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), 6.323 (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 $C_{25}H_{28}O_4$: 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 dienone *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,bs), 6.27 (1H,bs), 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 $C_{25}H_{26}O_4$: 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.[8] Chromatography of the methanol soluble part gave starting materials; 4,4′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl, 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), 3.99 (3H,s), 3.85 (6H,s), 2.88 (3H,s), 2.85 (3H,s), and 2.48 (6H,s) ppm, and anal. calc. for $C_{26}H_{28}O_4$: C 77.2, H 6.9. Found: C 77.5, H 6.8; the dienone *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), 2.72 (3H,s), 1.95 (6H,s), and 1.35 (3H,s) ppm, IR ν 1670 cm^{-1} (carbonyl), and anal. calc. for $C_{25}H_{26}O_4$: C 76.9, H 6.7. Found C t 6.7, 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 7.95 (1H,s), 7.83 (1H,s), 7.63 (1H,s), 7.50 (1H,s), 7.45 (1H,s), 4.03 (12H,s), 3.82 (3H,s), 2.83 (3H,s), and 2.48 (3H,s) ppm, and anal. calc. for $C_{25}H_{26}O_5$: C 73.9, H 6.4. Found: C 74.0, H 6.3. If the electrolysis was carried out in pure TFA no dienone (*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′-dimethylbiphenyl as the only product.

Coelectrolysis of 3,3′,4,4′-tetramethoxybiphenyl (*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. ($EtOH - CHCl_3 = 2:1$) 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 ($J_{H-12} = 9.17$ Hz, $J_{H-9} = 2.45$ Hz)), 3.958 (3H,s), 3.924 (3H,s), 3.921 (6H,s), and 3.907 (3H,s) ppm. Anal. calc. for $C_{23}H_{22}O_5$: 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′-dimethoxybiphenyl (0.20 g).

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