Electro-organic reactions. Part 51.† Reactivity and stereochemical pathways for cathodically generated radical-anions of α,β-unsaturated ketones in aqueous media

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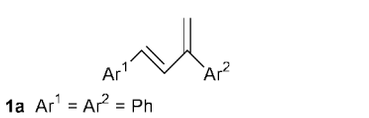
The cathodic reduction of α,β-unsaturated ketones in aqueous electrolyte gives efficient C–C coupling with the high stereoselectivity associated with similar reactions in aprotic media. The key features of these reactions are consistent with those expected from the likely mechanism involving water-templated coupling of radical-anions. As a further consequence the stereochemistry of the major products (cyclopentanols and linear hydrodimers) has been unambiguously assigned using X-ray crystallography and 2D NOESY ^{1}H NMR experiments.

Introduction

Important electrosynthetic reactions of activated alkenes involve carbon–carbon bond formation which, after much controversy, is now believed generally to involve radical-anion/radical-anion coupling rather than the alternative radical-anion/substrate reaction. The history of this mechanistic debate has been well-reviewed.[1] In a programme aimed at cleaner synthesis we are exploring the scope of electrosynthesis in aqueous media. Important examples of such reactions in protic solvents include *e.g.* the Monsanto process for the conversion[2–5] of acrylonitrile into adiponitrile (electrohydrodimerisation, EHD) and the reduction of cinnamate esters, which proceeds differently in aprotic[6] (DMF) and in protic solvents[7] (MeOH). In DMF, the major products are the all-*trans* 2-alkoxycarbonyl-3,4-diphenylcyclopentanones whereas from methyl cinnamate in MeOH, linear hydrodimers [(±) and *meso* isomers of dimethyl 3,4-diphenyladipate in statistical ratio] are formed together with 3-phenylpropionate, the product of cathodic hydrogenation.

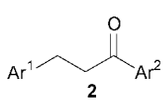
α,β-Unsaturated ketones reportedly[8] follow a somewhat different pattern and in aprotic media are electroreduced to oligomers, although an earlier paper reported[9] the formation from chalcone of cyclopentanols **3** *via* cyclic hydrodimerisation (CHD) [Scheme 1, **1a** ($Ar^1 = Ar^2 = Ph$)]. Other products may



1a $Ar^1 = Ar^2 = Ph$

1b $Ar^1 = 4\text{-}MeOC_6H_4$, $Ar^2 = Ph$

1c $Ar^1 = 4\text{-}MeOC_6H_4$, $Ar^2 = 2,4,6\text{-}Me_3C_6H_2$



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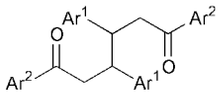
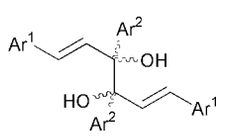


meso and (±)-**4**



meso and (±)-**5**

include the saturated ketones **2** (*via* radical-anion protonation), the hydrodimers **4**, formed as (±) and *meso* isomers *via* linear hydrodimerisation (LHD), and the pinacol **5**.

† For Part 50, see S. Szunerits, J. H. P. Utley and M. F. Nielsen, *J. Chem. Soc.*, *Perkin Trans. 2*, 2000, 669.

For cathodic reduction[8,10,11] of **1** (Scheme 1), cyclopentanols **3** are the main products and of the 16 possible isomers 8 have been postulated as products, the pairs of enantiomers **3A**–**3D**. Electrochemical reduction in the presence of metal cations[8] supposedly led to **3A** and **3B**, whereas chemical reduction[12–14] gave **3C** and **3D**.

The stereochemical diversity of products of LHD and of CHD, and the ability to perform these reactions in aqueous solution, makes them ideal candidates for further exploration with a view to ascertaining whether the high stereoselectivity found for aprotic conditions can be retained in aqueous media and, if so, whether stereoselectivity is determined by similar factors. Another issue to be resolved is that of the previously reported stereochemical outcomes which are inconsistent with recent mechanistic hypotheses.[1,6,7] In particular, cyclopentane derived products are expected[1] to have the less strained (±) coupling at C-3 and C-4, not the *meso* arrangement reported[8] (Scheme 1, isomers **3A** and **3B**).

Results and discussion

Preparative electrochemistry

Results for the electroreductions of the α,β-unsaturated ketones in polar aprotic and in protic media are compared (Table 1). A relatively high concentration of electrolyte (Et_4NOTs, 0.5 M) was used to enhance both miscibility of $BuOH–H_2O$ and to improve solubility of the organic substrates. In DMF only intractable polymers were formed, except from the more hindered **1c**. This gave smooth reduction to **2** and the hydrodimers, (±) and *meso* **4c**; in DMF–H_2O (10 equivalents) the pinacol **5** was formed in low yield (7%). Electrolyses carried out in *n*-butanol–water are much cleaner for all substrates. Both hydrogenation and hydrodimerisation were observed but, as expected for a second-order reaction, the proportion of C–C coupling (hydrodimerisation) increases with the initial concentration of the starting material.

Radical-anion coupling in aqueous media, despite competition from protonation, is well established and is associated[15] with the use of lipophilic electrolytes that arguably create an hydrophobic environment at the cathode. However, the cathodic reduction[7] of methyl cinnamate in MeOH gave only linear hydrodimers (*meso* and (±)). In contrast the radical-anions of α,β-unsaturated ketones couple in the aqueous medium with subsequent cyclisation, which is curious given their similar reactivity in DMF. In aprotic conditions [DMF–

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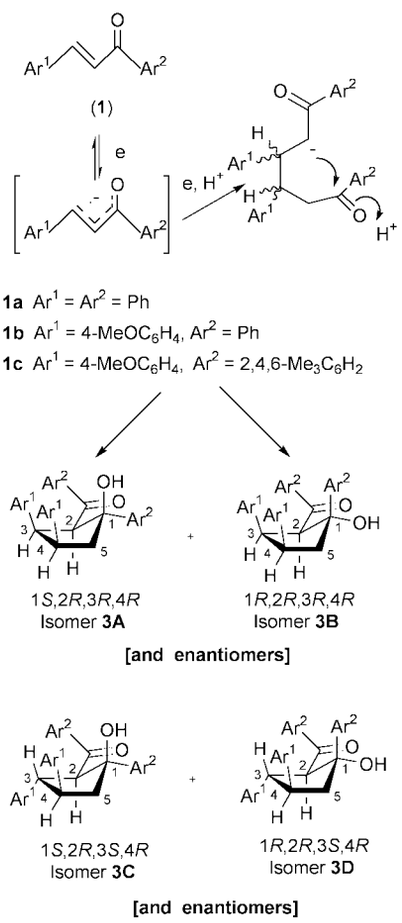
Table 1 Cathodic reduction of the α,β-unsaturated ketones **1** (see Scheme 1)

Cpd.	Reaction conditions[a]					Products [molar ratios]			Total yield[b] (%)
	Solvent[c]	$-E_p$[d]	$-E_{red}$	Charge/F	Concn/mM	**2**	Isomer of **3**	Isomer of **4**	
1a	DMF[e]	1.46	1.3	1.07	30	traces	traces	—	—
	H_2O–BuOH	1.43	1.3	1.07	60	[2.4]	**3C** [7.0] **3D** [1.0]	*meso* [trace]	86
1b	DMF	1.46	1.4	1.7	60	traces	traces	—	—
	H_2O–BuOH	1.46	1.3	1.1	60	[1.5]	**3C** [2.4] **3D** [trace]	*meso* [1.0]	83
1c	DMF	1.66	1.4	1.9	30	[22.7]	—	(±) [7.8] *meso* [1.0]	80[e]
			1.5	1.2	40	traces	—	(± [15.0] *meso* [1.0]	44[f]
	H_2O–BuOH	1.66	1.5	1.6	15	[7.2]	—	(±) [2.4] *meso* [1.0]	78
				1.1	60	[2.7]		(±) [5.1] *meso* [1.0]	65

[a] Divided cell, Hg pool cathode, graphite anode. [b] Aqueous work-up, extraction into EtOAc, pure products isolated by flash chromatography [Merck flash silica, cyclohexane–EtOAc (4:1)]. [c] DMF–Et_4NOTs (0.1 M) or *n*-BuOH–H_2O (2:3 v/v)–Et_4NOTs (0.5 M). [d] V *vs.* SCE. [e] HOAc to pH *ca.* 5.0 (moist pH paper). [f] 10 equivs. of H_2O, includes **5** (7%).



Scheme 1 Reported stereochemical outcomes of reduction of α,β-unsaturated ketones **1**.

Et_4NBr (0.1 M), Hg microelectrode] we determined the rate of dimerisation of the radical-anion of **1c** (Ar^1 = Ph, Ar^2 = 2,4,6-$Me_3C_6H_2$) to be $(1.05 \pm 0.06) \times 10^3$ dm^3 mol^{-1} s^{-1} and for methyl cinnamate $(5.97 \pm 0.50) \times 10^2$ as measured by cyclic voltammetry at various scan rates, with subsequent simulation (Bioanalytical Systems DigiSim 2.2 software). Literature[6] values for comparable reaction conditions are methyl cinnamate, $(7.8 \pm 0.7) \times 10^2$, and phenyl cinnamate, $(8.1 \pm 0.4) \times 10^3$. These reactions are much faster in protic solution[7] and we could not make comparable measurements in the aqueous solution. An important finding of this work is that the high

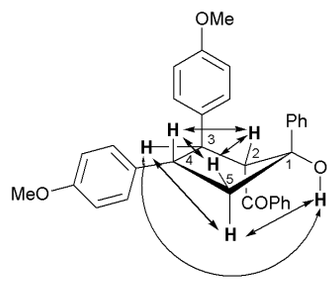


Fig. 1 Selected 2-D NOESY correlation for **3C** (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph).

stereoselectivity found for EHD with cyclisation for cinnamate esters[6] in DMF, is reproduced in reduction of the α,β-unsaturated ketones in aqueous media. This suggests that templating[6] of the radical-anions by water molecules is sufficiently strong to allow rapid and stereoselective coupling at C-3 and C-4 of the developing product, in effective competition with protonation. For **1c** similar hydrogen bonding with water is hindered by the bulky mesitylene group and consequently the linear hydrodimers **4** and **5** predominate in both (±) and *meso* forms.

Assignment of stereochemistry for the cyclopentanols 3 and linear hydrodimers 4

We conclude that the isomers of the cyclopentanols formed by both chemical and cathodic reduction correspond to the expected (±) coupling at C-3 and C-4 (Scheme 1, isomers **3C** and **3D**). One of the major cyclopentanol products of reduction of chalcone **1a** in the presence of metal cations[8] [mp 195 °C], was assigned the relative stereochemistry of the isomer **3A**; only one of the enantiomers is shown in Scheme 1. One of the products obtained by chemical reduction of **1a** had the same mp, but was assigned the stereochemistry of **3C**. We find that reduction of **1a** (see Table 1 for conditions) gives **3C** [mp 191–193 °C] with a second product being **3D** [mp 206.5–207.5 °C]. Comparison of ^{1}H NMR spectroscopic data allowed comparisons with the products found in earlier studies, notwithstanding the original faulty assignments of stereochemistry.

2-D NOESY correlation of the ^{1}H NMR spectrum of one of the cyclopentanol isomers obtained by reduction of **1b** showed strong interproton correlations (Fig. 1) indicating structure **3C** (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph), the result of the expected (±) coupling at C-3 and C-4. Compelling confirmation comes from the X-ray crystallographic determination[16] (Fig. 2a) of the structure of **3C** (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph). The NMR of

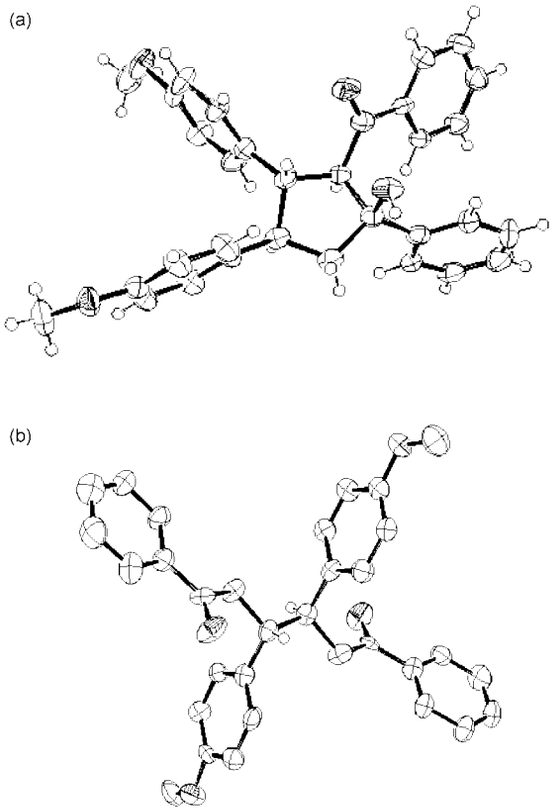


Fig. 2 (a) X-Ray crystallographic structure of **3C** (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph). (b) X-Ray crystallographic structure (partial determination, see text) of **4b** (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph).

3C (Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph), the structure now known with certainty, allows unambiguous assignment of the NMR data for other cyclopentanol products, including that of the product with mp 191–193 °C. Hence, both electrochemical and chemical reduction give the same two stereoisomeric cyclopentanols. The *meso* isomer of hydrodimer **4b** crystallised and, although the X-ray crystallographic[16] experimental data was weak, a partial structure determination was possible sufficient to specify the stereochemistry (Fig. 2b); this allowed confident assignment of ^{1}H NMR for all isomers of **4a**–**c**.

Experimental

Melting points were determined on a Reichert melting point apparatus and are uncorrected. Infrared spectra were recorded as liquid film or KBr disc on a Shimadzu FTIR-8300. ^{1}H NMR spectra were recorded on a Bruker AM250 (250 MHz) and AMX600 (600 MHz) spectrometers in $CDCl_3$ solvent with TMS as an internal standard. Preparative column chromatographic separations were performed on Merck silica gel 60H (230–400 mesh), while precoated silica gel plates (Merck, 60 F_{254}) were used for the analytical TLC. EI mass spectra were measured using a Kratos MS50RF/Kratos DS90 data system, and FAB mass spectra were obtained using *m*-nitrobenzyl alcohol as a matrix.

Solvents for cyclic voltammetric experiments were DMF (Aldrich, HPLC grade) and *n*-butanol (BDH, Analar grade). Tetraethylammonium bromide was used as electrolyte and potentials were measured against SCE. All cyclic voltammetric experiments were carried out using 2 mM solutions in an undivided cell with a polished gold cathode (1 mm diameter) and platinum coil counter electrodes.

Starting materials

The α,β-unsaturated ketones **1** were prepared by treatment of aromatic aldehydes with suitable ketones in aqueous ethanol in the presence of 10% NaOH in accordance with the reported method.[17] All starting materials were purified by column chromatography on silica gel and/or recrystallised from cyclohexane–ethyl acetate and the structures were verified by mass spectrometry, ^{1}H NMR and IR spectroscopy, and by comparison of melting points with literature melting values.[18–20]

General method for constant potential electrolyses

A glass cell was used for constant potential electrolysis with the cathode (stirred mercury pool, 16 cm² area) and anode (graphite) compartment separated by medium porosity glass sinter. The reference electrode was SCE. The reaction was kept in an inert atmosphere by the slow bubbling of nitrogen through the solution. The compound **1a**–**c** (1–4 mmol) was added to an efficiently stirred solution of electrolyte, (Et_4NOTs, 0.5 M) in *n*-BuOH–H_2O (2:3), in the working compartment (*ca.* 40 ml capacity) and the solution electrolysed at −1.3 to −1.5 V *vs.* SCE. Electrolysis was stopped when the current returned to a low background value. The catholyte was evaporated to dryness and the residue diluted with water (50 ml) and extracted with EtOAc (3 × 50 ml). The combined extract was washed with brine (2 × 40 ml), dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure to give a syrup. The crude product was purified by separation using flash chromatography with cyclohexane–EtOAc (4:1) as solvent to give **2**, **3**, **4**, and **5**.

Preparative scale electroreduction in DMF solutions was carried out similarly.

Electroreduction of 1,3-diphenylprop-2-en-1-one (1a)

Reduction of **1a** in *n*-BuOH–H_2O gave **2a**, **3a** (isomer **C** and isomer **D**) in 2.4:7.0:1.0 molar ratio, respectively, and traces of **4a**, in 86% overall yield. Similar reaction in polar aprotic solvent DMF gave polymeric materials and only traces of the above products.

1,3-Diphenylpropan-1-one (2a). MS (70 eV): *m*/*z* 210 (M^+), 105 (PhCO); mp 71–73 °C (lit.[19] 72–73 °C); ^{1}H NMR (250 MHz, $CDCl_3$, ppm): 7.15–7.95 (10H, m, Ar-H), 3.29 (2H, t, *J* 7.5 Hz, H-2), 3.06 (2H, t, *J* 7.5 Hz, H-3).

(1*S*,2*R*,3*S*,4*R*)-1,3,4-Triphenyl-2-benzoylcyclopentanol and enantiomer (3a, isomer C). MS (70 eV): *m*/*z* 400 ($M^+ - 18$), 295 [$M^+ - (18 + PhCO)$]; mp 191–193 °C (lit.[12] 192–194 °C); IR (liq. film, *ν*/cm^{-1}): 3436 (OH), 1640 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.00–7.60 (20H, m, Ar-H), 5.20 (1H, s, OH, exchangeable), 4.53 (1H, d, *J* 12.4 Hz, H-2), 4.10 (1H, dd, *J* 12.4, 10.0 Hz, H-3), 3.75–3.8 (1H, 6 lines, H-4), 2.99 (1H, ddd, *J* 14.5, 11.2, 1.2 Hz, H-5′), 2.58 (1H, dd, *J* 14.5, 6.2 Hz, H-5).

1*R*,2*R*,3*S*,4*R*)-1,3,4-Triphenyl-2-benzoylcyclopentanol and enantiomer (3a, isomer D). MS (70 eV): *m*/*z* 400 ($M^+ - 18$), 295 [$M^+ - (18 + PhCO)$]; mp 227–230 °C (lit.[21] 229–231 °C); IR (liq. film, *ν*/cm^{-1}): 3500 (OH), 1655 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.05–7.45 (20H, m, Ar-H), 4.51 (1H, d, *J* 5.5 Hz, H-2), 3.93–3.99 (2H, m, H-3 and -4), 3.14 (1H, dd, *J* 12.8, 10.8 Hz, H-5), 2.36 (1H, dd, *J* 12.8, 5.0 Hz, H-5), 2.10 (1H, s, OH, exchangeable).

(3*S*,4*R*)-1,3,4,6-Tetraphenylhexane-1,6-dione (4a, *meso*). MS (70 eV): *m*/*z* 418 (M^+), 209 (M^+/2); mp 270–272 °C (lit.[22] 272–273 °C), IR (liq. film, *ν*/cm^{-1}): 1682 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.0–7.60 (10H, m, Ar-H), 3.71–3.75 (1H, m, H-3 and -4), 3.31 (1H, dm, *J* 14.7 Hz, H-2 and -5), 2.93 (1H, dm, *J* 14.7 Hz, H-2 and -5).

Electroreduction of 1-phenyl-3-(4′-methoxyphenyl)prop-2-en-1-one (1b)

Electrolysis in DMF containing HOAc (pH *ca.* 5.0), gave only trace amounts of identifiable hydrogenation product **2b** and

cyclic hydrodimers **3b** as detected by ^{1}H NMR spectroscopy and the rest were polymeric materials. In *n*-BuOH–H_2O, a similar reaction resulted in the formation of **2b**, **3b** (isomer **C**), a small amount of **3b** (isomer **D**), and traces of **4b**, in an overall yield of 83%.

1-Phenyl-3-(4′-methoxyphenyl)propanone (2b). MS (70 eV): *m*/*z* 240 (M^+), 121 (C_8H_9O), 105 (PhCO); mp 66–68 °C (lit.[23] 67–68 °C); IR (liq. film, *ν*/cm^{-1}): 1681 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.84–7.95 (9H, m, Ar-H), 3.29 (3H, s, OMe), 3.27 (2H, t, *J* 10 Hz, H-2), 3.03 (2H, t, *J* 10 Hz, H-2).

(1*S*,2*R*,3*S*,4*R*)-1-Phenyl-3,4-bis(4′-methoxyphenyl)-2-benzoylcyclopentanol and enantiomer (3b, isomer C). MS (70 eV): *m*/*z* 460 ($M^+ - 18$), 355 [$M^+ - (18 + PhCO)$]; IR (liq. film, *ν*/cm^{-1}): 3435 (OH), 1681 (CO); mp 167–168 °C; ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.64–7.55 (18H, m, Ar-H), 5.17 (1H, s, OH, exchangeable), 4.47 (1H, d, *J* 12.3 Hz, H-2), 4.00 (1H, dd, *J* 12.3, 9.8 Hz, H-3), 3.75 (3H, s, OMe), 3.65 (3H, s, OMe), 3.63–3.69 (1H, m, H-4), 2.96 (1H, ddd, *J* 14, 9.8, 1.2 Hz, H-5′), 2.16 (1H, dd, *J* 14, 6.3 Hz, H-5).

Crystallography

The intensity data were collected on an Enraf Nonius CAD-4 diffractometer using Mo-Kα radiation (*λ* 0.71069 Å) with an *ω*–2*θ* scan at 120 K. The unit cell parameters were determined by least-squares refinement on diffractometer angles $8.02 \leq \theta \leq 12.22°$ (**3C**) and $9.01 \leq \theta \leq 13.08°$ (*meso*-**4b**) for 25 automatically centred reflections in each case.[24] All data were corrected for absorption by semi-empirical methods (ψ scan)[25] and for Lorentz-polarization effects by XCAD4.[26] The structure was solved by direct method using SHELXS-97,[27] and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2 using the SHELXL-97 program.[27] The H atoms were calculated geometrically and refined with a riding model. The high residual-factor in the refinement of the structure of the linear hydrodimer **4b** (Fig. 2b) can be attributed mainly to disorder in an associated solvent molecule ($CHCl_3$) in addition to the limited number of strong reflections from a small crystal. The dominant atomic scatterer is Cl, which makes a large contribution to the overall scattering from the crystal. In this case positional ambiguity through disorder has a large effect on the residual factor. Despite this, the molecule of interest is sufficiently well resolved for the assignment of stereochemistry to be secure. Despite efforts to model the disorder entity (refined in two staggered positions), the *R*-factor remained high. The program ORTEP-3[28] was used for drawing the molecules. WINGX[29] was used to prepare material for publication.

Crystal data. Structure of **3c**: $C_{32}H_{30}O_4$, $M = 478.56$, monoclinic, $a = 11.431(5)$, $b = 6.0470(10)$, $c = 18.286(6)$ Å, $U = 1255.4(7)$ Å^3, $T = 120$ K, space group $P2_1$, $Z = 2$, $\mu = 0.082$ mm^{-1}. The final $wR(F^2)$ was $R1 = 0.1431$, $wR2 = 0.1443$ (all data). Partial determination of structure *meso*-**4b**: $C_{33}H_{31}Cl_3O_4$ [includes molecule of $CHCl_3$], $M = 597.93$, monoclinic, $a = 21.396(8)$ Å, $b = 5.699(4)$ Å, $c = 24.090(9)$ Å, $T = 120$ K, space group $P2_1/n$. The final $wR(F^2)$ was $R1 = 0.1627$, $wR2 = 0.4387$.

(1*R*,2*R*,3*S*,4*R*)-1-Phenyl-3,4-bis(4′-methoxyphenyl)-2-benzoylcyclopentanol and enantiomer (3b, isomer D)

MS (70 eV): *m*/*z* 460 ($M^+ - 18$), 355 [$M^+ - (18 + PhCO)$]; IR (liq. film, *ν*/cm^{-1}): 3500 (OH), 1650 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.70–7.55 (18H, m, Ar-H), 4.46 (1H, d, *J* 5.0 Hz, H-2), 3.83–3.86 (2H, m, H-3 and -4), 3.79 (3H, s, OMe), 3.70 (3H, s, OMe), 3.08 (1H, t, 12.8 Hz, H-5), 2.33 (1H, dd, *J* 12.8, 5 Hz, H-5), 2.12 (1H, s, OH, exchangeable).

(3*S*,4*R*)-1,6-Diphenyl-3,4-bis(4′-methoxyphenyl)hexane-1,6-dione (4b, *meso*)

MS (70 eV): *m*/*z* 478 (M^+), 239 (M^+/2), 105 (PhCO); IR (liq. film, *ν*/cm^{-1}): 1680 (CO); mp 217–220 °C (lit.[22] 218–222 °C); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.81–7.46 (9H, m, Ar-H), 3.74 (3H, s, OMe), 3.58–3.63 (1H, m, H-3 and -4), 3.21 (1H, dm, *J* 16.2 Hz, H-2 and -5), 2.93 (1H, dd, *J* 16.2, 2.5 Hz, H-2′ and -5′).

Electroreduction of 1-mesityl-3-(4′-methoxyphenyl)prop-2-en-1-one (1c)

Constant potential electroreduction of **1c** in both polar aprotic and *n*-BuOH–H_2O solvent systems gave similar products, namely **2c** and the straight chain hydrodimers **4c**, (±) and *meso* isomers.

1-Mesityl-3-(4′-methoxyphenyl)propan-1-one (2c). MS (70 eV): *m*/*z* 282 (M^+), 147 [$(CH_3)_3C_6H_2CO$]; IR (liq. film, *ν*/cm^{-1}): 1696 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.81–7.14 (6H, m, Ar-H), 3.77 (3H, s, OMe), 2.98 (4H, s, H-2 and -3), 2.56 (3H, s, Me-*para*), 2.11 (6H, s, Me-*ortho*).

(3*S*,4*R*)-1,6-Dimesityl-3,4-bis(4′-methoxyphenyl)hexane-1,6-dione (4c, *meso*). MS (FAB): *m*/*z* 563 ($M^+ + 1$), 281 (M^+/2); IR (liq. film, *ν*/cm^{-1}): 1691 (CO); ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.66–7.26 (6H, m, Ar-H), 3.78 (3H, s, OMe), 3.51–3.57 (1H, m, H-3), 2.94 (1H, dm, *J* 19 Hz, H-2 and 5), 2.70 (1H, d, *J* 19 Hz, H-2′ and -5′), 2.18 (3H, s, Me-*para*), 1.63 (6H, s, Me-*ortho*).

(3*S*,4*R*)-1,6-Dimesityl-3,4-bis(4′-methoxyphenyl)hexane-1,6-dione [4c, (±)]. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 6.68–6.81 (6H, m, Ar-H), 3.74 (3H, s, OMe), 3.60–3.65 (1H, m, H-3), 3.10 (1H, dd, *J* 17.8, 8.9 Hz, H-2 and -5), 3.04 (1H, dd, *J* 17.8, 3.8 Hz, H-2′ and -5′), 2.23 (3H, s, Me-*para*), 1.90 (6H, s, Me-*ortho*).

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