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SYNTHESIS OF PHENYL SUBSTITUTED CYCLOHEXA-1,4-DIENES AND CYCLOHEXA-2,5-DIENONES BY ANODIC METHOXYLATION OF ALKYLBIPHENYLS[1]

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Abstract: The anodic methoxylation of a series of alkylbiphenyls (2-, 3-, 4-methylbiphenyl, 3,3'-, 4,4'-dimethylbiphenyl, 4-ethylbiphenyl and 4,4'-di-*tert*-butylbiphenyl) carried out under constant current intensity afforded, in a process of two electrons, a number of *cis/trans* cyclohexa-1,4-dienes and, in a process of four electrons, a number of cyclohexa-2,5-dienones after acidic hydrolysis of the corresponding cyclohexa-1,4-diene ketals. In some cases, side-chain substitution products were also obtained. Probable mechanisms are proposed.

Introduction

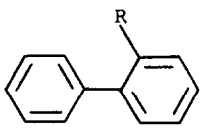
Nuclear methoxylation of aromatic compounds giving 1,2- and 1,4-addition products have been reported[2-4] for substrates in which the aromatic nucleus is always activated by alkoxy groups which stabilize the initial cation-radical intermediate. When there are alkyl groups attached to the aromatic ring, the proton loss from the side-chain is rapid and a side-chain substitution process competes strongly.[5] Nuclear attack occurs only if there is a strong nucleophile which can react sufficiently fast with the cation-radical to compete with deprotonation.

Our investigation on the anodic oxidation of alkylbenzenes by electrochemical methoxylation[6] led us to conclude that nuclear addition products such as the *cis/trans* and cyclohexa-1,4-diene ketals, could be obtained not only when the original substrates are activated benzenes. Recently,[7] we have studied the reactivity of a member of this rare class of compounds, the 3,6-dimethoxy-3,6- dimethylcyclohexa-1,4-diene, obtained in multigram scale from *p*-xylene,[6a] and found an adequate route to introduce oxygen-, sulfur- , or carbon-containing nucleophiles both in the ring or at the benzylic position of *p*-xylene.

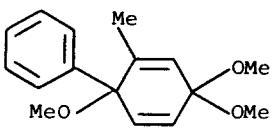
In the last years, a number of works have focused on the electrosynthesis of biphenylic cyclohexadiene rings,[8,9] but always through the anodic oxidation of oxygenated biphenyl systems. Nevertheless, the anodic oxidation chemistry of alkylbiphenyls is practically unknown. We report now the electrochemical oxidation of a number of alkylbiphenyls giving both nuclear addition and side-chain substitution products.

Results and Discussion

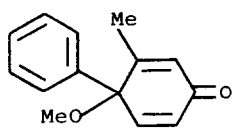
The anodic oxidation of 2-methylbiphenyl under constant current intensity led to the side chain substitution products **1** and **2**. The degree of side chain substitution increased with the current consumption. In addition to these products, the nuclear addition compound **3** was obtained. Acidic hydrolysis of **2** and **3** afforded the aldehyde **2a** and the cyclohexadienone **3a** in quantitative yield (in this work if an identified compound is denoted as **X**, its hydrolysis product will be denoted as **Xa**).



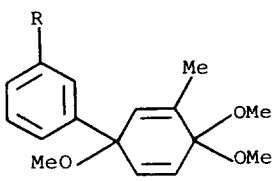
1 ; R=CH_2OMe
2 ; R=$CH(OMe)_2$
2a; R=CHO



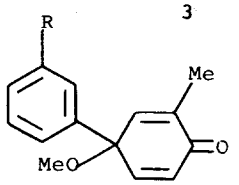
3



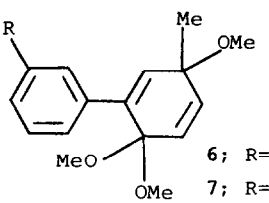
3a



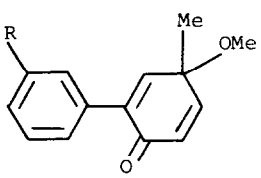
4; R=H
5; R=Me



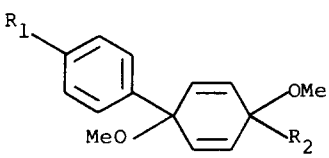
4a; R=H
5a; R=Me



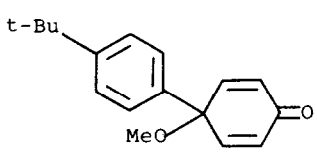
6; R=H
7; R=Me



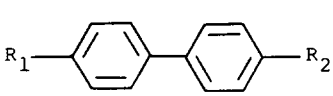
6a; R=H
7a; R=Me



8; R_1=H, R_2=Me
9; R_1=Me, R_2=Me
10; R_1=CH_2OMe, R_2=Me
11; R_1=$CH(OMe)_2$, R_2=Me
12; R_1=H, R_2=Et
13; R_1=Et, R_2=OMe
14; R_1=t-Bu, R_2=OMe



14a



15; R_1=H, R_2=CH_2OMe
16; R_1=H, R_2=$CH(OMe)_2$
17; R_1=H, R_2=$C(OMe)_3$
18; R_1=Me, R_2=CH_2OMe
19; R_1=Me, R_2=$CH(OMe)_2$
20; R_1=Me, R_2=$C(OMe)_3$
21; R_1=H, $R_2CHOMeCH_3$
22; R_1=H, R_2=$C(OMe)_2CH_3$

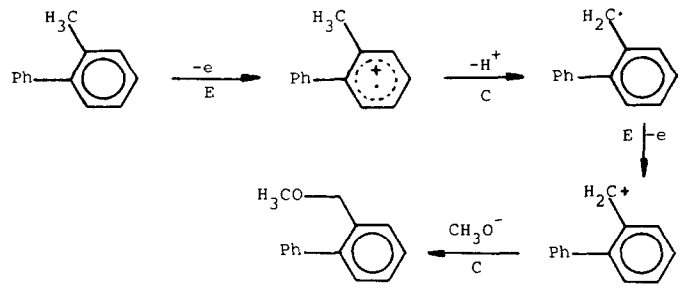
16a; R_1=H, R_2=CHO
17a; R_1=H, R_2=CO_2Me
19a; R_1=Me, R_2=CHO
22a; R_1=H, R_2=$COCH_3$

Table 1. Products and yields.

Initial substrate	Reaction time (min)	Product, yield (%)[a]
2-methylbiphenyl	90	**1**(10), **2**(39), **3**(8)
3-methylbiphenyl	45	**4**(52), **6**(6)
3,3'-dimethylbiphenyl	60	**5**(36), **7**(8)
4-methylbiphenyl	45	**8**(20)[b], **15**(4), **16**(33), **17**(7)
4,4'-dimethylbiphenyl	45	**9**(25)[c], **10**(5)[d], **11**(13)[e], **18**(1), **19**(3), **20**(1)
4-ethylbiphenyl	45	**12**(8)[f], **13**(5), **21**(12), **22**(29)
4,4'-di-*tert*-butylbiphenyl	60	**14**(19)

a) Deduced by g.l.c. analysis using cyclohexanone as internal standard. *Cis/trans* ratio: b) 1/1.7; c) 1/2.3; d) 1/1.8; e) 1/1.2; f) 1/1.9.

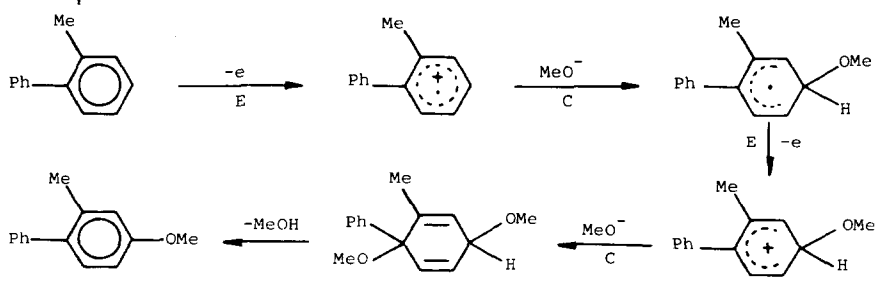
The obtention of compound **1** (and any side-chain methoxylated compound) can be easily explained through a classical ECEC sequence:[10]



Scheme 1

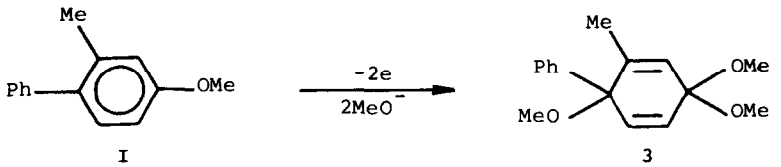
A new ECEC sequence leads to compound **2**.

The formation of compound **3** could be explained through the same sequence previously described for the obtention of the nuclear methoxylated products obtained in the anodic oxidation of *p*-xylene.[6a] But in this case, the *cis* and *trans* nuclear dimethoxylated products would not be stable and decompose to the intermediate compound **I**:



Scheme 2

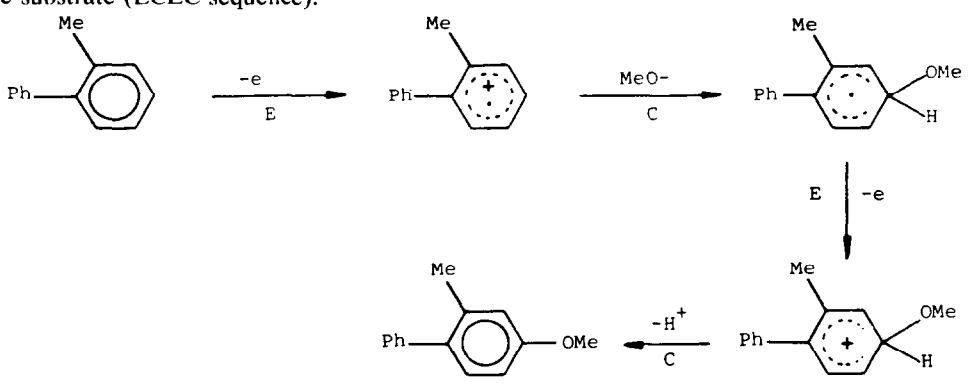
In compound **I**, the aromatic ring is activated by the methoxy group and leads rapidly to the nuclear trimethoxylated compound **3** through another methoxylation process:



I 3

Scheme 3

Another plausible pathway for the formation of the intermediate **I** consists of a nuclear methoxylation of the substrate (ECEC sequence):

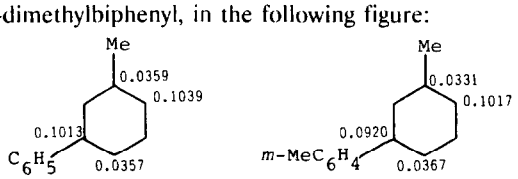


I

Scheme 4

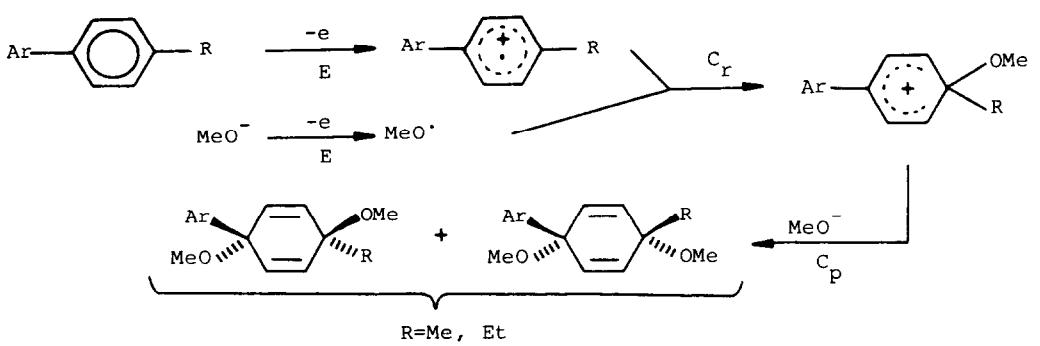
Both ways are possible, but the intermediate **I** was not detected in the reaction medium. This fact is indicative that the probable route is that shown in Scheme 4, because the compound **I**, which is formed on the electrode surface, is not deadsorbed and is re-oxidized to give **3**. If the reaction took place through an addition-elimination pathway as shown in Scheme 2, the compound **I** should be formed in the bulk of the solution and its concentration should be measurable.

The anodic methoxylation of 3-methylbiphenyl afforded the nuclear addition products **4** and **6**, whereas the methoxylation of 3,3'-dimethylbiphenyl gave **5** and **7**. The greater abundance of compounds **4** and **5** than **6** and **7** (see Table 1) is explained by the positive charge density at the different carbon atoms in the cation radical, whose highest values mark the position of the nucleophilic attack of the electrolyte. These positive charge densities (calculated by the MINDO/3 method[11]) are shown, for the cation radical of 3-methylbiphenyl and 3,3'-dimethylbiphenyl, in the following figure:



In this case, the mechanistic pathway proposed is of the ECEC type as mentioned above (see Scheme 4). It is worthy to note that side-chain methoxylated products are not detected, whereas they are the major products in the methoxylation of 2-methylbiphenyl.

The anodic methoxylation of 4-methylbiphenyl, 4,4'-dimethylbiphenyl and 4-ethylbiphenyl, led to the *cis* and *trans* nuclear addition isomers **8**, **9**, **10**, **11** and **12**, the cyclohexadienic ketal **13**, and a number of side chain oxidation products (see Table 1). The *cis* and *trans* structures of compound **8** were assigned by comparison of its ^{1}H NMR spectral data with those of the *trans*-3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene, unequivocally identified by X-ray diffraction.[6d] These assignations were confirmed by ammonia chemical ionization mass spectrometry because the higher abundance of the $[M+NH_4]^+$ ion in the previously assigned *cis* isomer than in the *trans* isomer, which has been justified by the formation of a more stable proton-bond adduct, $[M+NH_4]^+$, in the *cis* isomers of the 3,6-dimethoxycyclohexa-1,4-dienes.[12] Comparison of the ^{1}H NMR signals of the *cis/trans* isomers **9**, **10**, **11** y **12** with those of the isomers **8** let us assign its structures. The formation of these *cis* and *trans* isomers could be explained through the same sequence described in Scheme 2. A more recent mechanistic proposal[6d,13] favors a sequence involving methoxy radical attack on the aryl cation radical. This sequence is termed EEC_rC_p (C_r and C_p refer to chemical steps involving radical and polar intermediates, respectively). In this case the electrode surface does not influence the formation of a determined isomer and the isomeric ratio should be the same. This route is shown in the following scheme:



Scheme 5

The ratio *cis/trans* obtained (see Table 1), always shows a higher abundance of the *trans* isomer than the *cis* isomer. Thus, the preferred mechanism is a ECEC sequence (see Scheme 2), and the isomeric ratio could be explained by stereocontrol of the electrode surface in the nucleophilic attack (MeO^-) on the cation intermediate, which would be situated on the electrode with the methoxyl group oriented towards the anode surface. A extreme case of this minor selectivity for the *cis* isomers has been observed in the anodic methoxylation of pseudocumene, which afforded only the *trans* isomer of the 3,6-dimethoxy-1,3-6-trimethylcyclohexa-1,4-diene.[6c]

The electrooxidation of 4,4'-di-*tert*-butylbiphenyl gave the nuclear addition compound **14**, product of the elimination of a *tert*-butyl group. The obtention of this compound can be justified by means of the elimination of a *tert*-butyl cation, instead of a proton, in the last step of Scheme 4 and then, another process of two electrons (see Scheme 3).

It is worthy to note that in the electrooxidation of all the alkylbiphenyls studied, we have only observed the nuclear addition process in an aromatic ring. The lack of attack on the second ring might be a surface phenomenon that could be explained considering the geometric change in the molecule when the cyclohexadienic system is formed. Thus, the relative planarity between the rings is modified, and the second adsorption on the electrode surface would be more difficult.

Conclusions

We conclude that the anodic methoxylation of alkylbiphenyls under constant current intensity is an interesting route for the functionalization of such systems. This method allows the obtention of new cyclohexadienic compounds, along benzylic methoxylation products.

Experimental

A Promax generator with a maximum output of 60 V and 2 A was used. Melting points were measured on a Reichert Thermovar hot-stage microscope and were uncorrected. IR spectra were measured as films or as KBr discs for solids on a Pye Unicam SP3-200. ^{1}H NMR spectra were recorded at 60 MHz on a Varian EM-360L spectrometer in deuteriochloroform as solvent. The chemical shifts are expressed in parts per million downfield from internal tetramethylsilane (TMS, $\delta = 0$). Mass spectra (EI) were recorded on a HP-5988A spectrometer at 70 eV. A Perkin-Elmer 240 microanalyzer was used. Gas liquid-phase chromatographic (g.l.c.) analyses were performed on a HP-5890 instrument (OV-101, 25 m x 0.22 mm column) equipped with a flame ionization detector, using nitrogen as the carrier gas (2 mL/min), $T_{injector} = 250°C$, $T_{column} = 170°C$ (1 min) and 170-240°C (7°C/min); retention times (t_r) are given under these conditions. For flash column chromatography was used silica gel Merck Kieselgel 60 (Art. 9385).

General procedure.- Electrolyses were carried out in cylindrical, water-refrigerated cells without separate compartments. The temperature was controlled at 30°C and stirring was magnetic. A carbon paste plate was used as the anode and a stainless-steel plate as the cathode. Reactions with the initial substrates (0.3 g) were carried out under a constant current intensity of 1 A with an anodic density of 57 mA cm^{-2}. The solvent was dry methanol (70 mL) and the electrolyte was sodium methoxide (0.2 g). At the end of each electrolysis (followed by TLC), the solution was worked up by evaporation of the solvent to dryness under reduced pressure. The extract was suspended in 100 mL of water (electrolysis of 4-methylbiphenyl, 4,4'-dimethylbiphenyl and 4-ethylbiphenyl) or a buffer solution of KH_2PO_4/Na_2HPO_4 (0.025 M) (electrolysis of 2-, 3-methylbiphenyl, 3,3'-dimethylbiphenyl and 4,4'-di-*tert*-butylbiphenyl), and extracted with ethylic ether (3 x 30 mL). The combined organics were dried with anhydrous sodium sulfate and the ether was evaporated at reduced pressure. Products were isolated by flash chromatography using hexane/ethyl acetate (98:2 v/v) as eluent (electrolysis of 4-methylbiphenyl, 4,4'-dimethylbiphenyl and 4-ethylbiphenyl), or by chromatography on a neutral carbon-celite column and ethylic ether as eluent (electrolysis of 2-, 3-methylbiphenyl, 3,3'-dimethylbiphenyl and 4,4'-di-*tert*-butylbiphenyl).

Acidic hydrolysis were carried out dissolving the compounds in ethylic ether and adding to the mixture a solution of 50% hydrochloric acid. The mixture was stirred and the organic layer dried over anhydrous sodium sulfate and evaporated *in vacuo*. Hydrolysis products were obtained in quantitative yield.

Impurified or low-yield products could be characterized by tandem g.l.c.-mass spectrometry. *Trans* isomers were isolated, whereas *cis* isomers were identified in the *cis/trans* mixture. Isolated yields for pure compounds, based on the crude extract, are given.

2-(Methoxymethyl)biphenyl (**1**). Colourless oil (7% yield). t_r=6.42 min; IR ν_{max} 3060, 3020, 1600, 770, 750, 700 cm^{-1}; ^1H NMR δ 7.40 (m, 9H), 4.35 (s, 2H), 3.30 (s, 3H); MS m/z 198 (M', 57%), 167 (35), 166 (43), 165 (100), 152 (29), 121 (10), 115 (10), 77 (11). Anal. calc for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.88; H, 7.16.

2-(Dimethoxymethyl)biphenyl (**2**). Colourless oil (30% yield). t_r=7.23 min; IR ν_{max} 3060, 3020, 1600, 1090, 1070, 1050, 760, 750, 700 cm^{-1}; ^1H NMR δ 7.40 (m, 9H), 5.15 (s, 1H), 3.25 (s, 6H); MS m/z 228 (M', 11%), 198 (43), 197 (37), 181 (21), 165 (100), 153 (29), 152 (39), 128 (11), 115 (15), 77 (12), 75 (13). Anal. calc for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.82; H, 7.00.

2-Phenylbenzaldehyde (**2a**). Colourless oil. t_r=7.58 min (lit.,[14] b.p. 150°C/7 torr); IR ν_{max} 3060, 3020, 1680, 1600, 750, 700 cm^{-1}; ^1H NMR δ 10.00 (s, 1H), 7.45 (m, 9H); MS m/z 182 (M', 76%), 181 (100), 153 (72), 152 (92), 151 (35), 126 (16), 115 (20), 87 (11), 77 (13), 74 (27), 51 (29).

3,6,6-Trimethoxy-2-methyl-3-phenylcyclohexa-1,4-diene (**3**). t_r=8.16 min; MS m/z 260 (M', 55%), 245 (45), 229 (97), 228 (38), 214 (100), 198 (59), 185 (49), 183 (30), 169 (31), 155 (45), 153 (80), 152 (60), 141 (36), 128 (78), 115 (90), 91 (42), 77 (38), 65 (35).

4-Methoxy-3-methyl-4-phenylcyclohexa-2,5-dienone (**3a**). Colourless oil. t_r=7.58 min. IRν_{max} 3020, 2820, 1660, 1630, 1070, 880, 760, 700 cm^{-1}. ^1H NMR δ 7.35 (m, 5H), 6.70 (m, 2H), 6.40 (m, 1H), 3.30 (s, 3H), 1.75 (d, 3H, J=1.5 Hz). MS m/z 214 (M', 34%), 199 (29), 186 (50), 182 (12), 171 (100), 159 (16), 153 (36), 152 (27), 143 (24), 128 (68), 115 (57), 105 (23), 103 (26), 77 (67), 63 (26), 51 (48). Anal. calc. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.39; H, 6.65.

3,6,6-Trimethoxy-1-methyl-3-phenylcyclohexa-1,4-diene (**4**). Colourless oil (44% yield). t_r=8.38 min; IR ν_{max} 3060, 2820, 1080, 750, 680, 690 cm^{-1}; ^1H NMR δ 7.35 (m, 5H), 6.15 (m, 2H), 5.85 (m, 1H), 3.35 (s, 3H), 3.30 (s, 3H), 3.20 (s, 3H), 1.85 (d, 3H, J=1.5 Hz); MS m/z 260 (M', 28%), 245 (48), 229 (100), 214 (58), 198 (39), 185 (41), 184 (85), 183 (54), 165 (23), 153 (33), 152 (30), 141 (12), 128 (26), 115 (29), 105 (10), 77 (26), 51 (12). Anal. calc. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.86; H, 7.71.

4-Methoxy-2-methyl-4-phenylcyclohexa-2,5-dienone (**4a**). Colourless oil. t_r=6.99 min; IRν_{max} 3060, 2820, 1670, 1640, 1070, 890, 820, 750, 700 cm^{-1}; ^1H NMR δ 7.35 (m, 5H), 6.75 (dd, 1H, J_1=10 Hz, J_2=3 Hz), 6.55 (m, 1H), 6.35 (d, 1H, J=10 Hz), 3.40 (s, 3H), 1.95 (d, 3H, J=1.5 Hz); MS m/z 214 (M', 95%), 199 (32), 186 (50), 183 (27), 171 (100), 153 (43), 143 (33), 128 (79), 115 (48), 103 (13), 77 (41), 51 (23). Anal. calc. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.41; H, 6.61.

3,6,6-Trimethoxy-1-methyl-3-(3-methylphenyl)cyclohexa-1,4-diene (**5**). Colourless oil (29% yield). t_r=9.32 min; IR ν_{max} 3020, 2820, 1600, 1080, 820, 780, 700, 680 cm^{-1}; ^1H NMR δ 7.20 (m, 4H), 6.15 (m, 2H), 5.85 (m, 1H), 3.35 (s, 3H), 3.30 (s, 3H), 3.20 (s, 3H), 2.35 (br s, 3H), 1.85 (d, 3H, J=1.5 Hz); MS m/z 274 (M', 33%), 259 (40), 243 (100), 242 (93), 228 (54), 227 (48), 212 (78), 199 (35), 197 (40), 165 (26), 153 (30), 152 (34), 141 (21), 115 (31), 91 (29), 89 (19), 77 (17), 65 (19). Anal. calc. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.51; H, 8.02.

4-Methoxy-2-methyl-4-(3-methylphenyl)cyclohexa-2,5-dienone (**5a**). Colourless oil. t_r=7.96 min; IRν_{max} 3020, 2820, 1660, 1640, 1600, 1070, 880, 810, 780, 690 cm^{-1}; ^1H NMR δ 7.25 (m, 4H), 6.75 (dd, 1H, J_1=10 Hz, J_2=3 Hz), 6.55 (m, 1H), 6.35 (d, J=10 Hz), 3.40 (s, 3H), 2.35 (br s, 3H), 1.95 (d, 3H, J=1.5 Hz); MS m/z 228 (M', 91%), 213 (37), 200 (29), 197 (28), 196 (24), 185 (100), 181 (21), 169 (10), 167 (14), 165 (13), 157 (28), 153 (41), 152 (33), 142 (45), 141 (31), 128 (30), 115 (47), 91 (37), 77 (25), 65 (34), 63 (26), 51 (23). Anal. calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: 78.87; H, 7.11.

3,6,6-Trimethoxy-3-methyl-1-phenylcyclohexa-1,4-diene (**6**). t_r=8.91 min; MS m/z 260 (M', 62%), 245 (32), 229 (100), 214 (98), 198 (40), 185 (36), 183 (27), 165 (10), 155 (26), 128 (27), 115 (26), 105 (10), 91 (14), 77 (12).

4-Methoxy-4-methyl-2-phenylcyclohexa-2,5-dienone (**6a**). Colourless oil. t_r=7.31 min; IRν_{max} 3060, 2820, 1660,

1630, 1080, 830, 690 cm^{-1}; ^1H NMR δ7.40 (m, 5H), 6.80 (m, 2H), 6.40 (d, 1H, J=10 Hz), 3.30 (s, 3H), 1.50 (s, 3H); MS m/z 214 (M', 75%), 199 (42), 186 (71), 183 (47), 171 (100), 168 (70), 153 (33), 143 (18), 128 (70), 115 (42), 102 (25), 91 (13), 77 (28), 51 (20). Anal. calc. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.44; H, 6.57.

3,6,6-Trimethoxy-3-methyl-1-(3-methylphenyl)cyclohexa-1,4-diene (**7**). t_r=9.08 min; MS m/z 274 (M', 60%), 259 (36), 243 (100), 228 (62), 213 (22), 212 (42), 199 (40), 197 (33), 185 (16), 183 (18), 167 (14), 165 (25), 154 (27), 153 (34), 152 (46), 141 (23), 137 (23), 128 (23), 115 (34), 105 (19), 91 (50), 77 (20), 65 (55).

4-Methoxy-4-methyl-2-(3-methylphenyl)cyclohexa-2,5-dienone (**7a**). Colourless oil. t_r=8.38 min; IR ν_{max} 3020, 2820, 1660, 1640, 1600, 830, 790, 740, 690 cm^{-1}; ^1H NMR δ 7.20 (m, 4H), 6.80 (m, 2H), 6.40 (d, 1H, J=10 Hz), 3.30 (s, 3H), 2.35 (br s, 3H), 1.50 (s, 3H); MS m/z 228 (M', 75%), 213 (56), 200 (58), 197 (41), 185 (100), 182 (58), 181 (53), 169 (15), 165 (14), 157 (18), 153 (30), 152 (32), 142 (30), 141 (28), 128 (22), 115 (61), 91 (15), 89 (15), 77 (18), 63 (27), 51 (25). Anal. calc. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.50; 8.01.

Cis *and* trans-*3,6-dimethoxy-6-methyl-3-phenylcyclohexa-1,4-diene* (**8**). Colourless oil (14% yield). *Cis* isomer t_r=7.08 min, *trans* isomer t_r=7.03 min; IR ν_{max} 3060, 3020, 2820, 1600, 1090, 1070, 880, 750, 690 cm^{-1}; *cis* isomer ^1H NMR δ 7.40 (m, 5H), 5.95 (s, 4H), 3.35 (s, 3H), 3.25 (s, 3H), 1.35 (s, 3H); *trans* isomer ^1H NMR δ7.40 (m, 5H), 5.95 (s, 4H), 3.20 (s, 3H), 3.15 (s, 3H), 1.40 (s, 3H); MS m/z 230 (M', 69%), 215 (68), 199 (100), 184 (89), 173 (28), 167 (43), 165 (47), 153 (63), 141 (37), 128 (25), 115 (53), 91 (26), 89 (23), 77 (46), 59 (25), 51 (19). Anal. calc. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.18; H, 7.90.

Cis *and* trans-*3,6-dimethoxy-6-methyl-3-(4-methylphenyl)cyclohexa-1,4-diene* (**9**). Colourless oil (20 % yield). *Cis* isomer t_r=7.08 min, *trans* isomer t_r=7.03 min; IR ν_{max} 3020, 2820, 1600, 1070, 810, 770, 660 cm^{-1}; *cis* isomer ^1H NMR δ7.45 (d, 2H, J=8 Hz), 7.15 (d, 2H, J=8 Hz), 5.95 (s, 4H), 3.30 (s, 3H), 3.25 (s, 3H), 2.35 (br s, 3H), 1.35 (s, 3H); *trans* isomer ^1H NMR δ 7.45 (d, 2H, J=8 Hz), 7.15 (d, 2H, J=8 Hz), 5.95 (s, 4H), 3.20 (s, 3H), 3.15 (s, 3H), 2.35 (br s, 3H), 1.40 (s, 3H); MS m/z 244 (M', 98%), 229 (41), 213 (100), 198 (72), 186 (28), 182 (27), 167 (22), 165 (47), 153 (40), 115 (22), 91 (20), 89 (16), 77 (13), 59 (13). Anal. calc. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.60; H, 8.22.

Cis *and* trans-*3,6-dimethoxy-3-[4-(methoxymethyl)phenyl]-6-methylcyclohexa-1,4-diene* (**10**). Colourless oil (2% yield). *Cis* isomer t_r=10.83 min, *trans* isomer t_r=10.75 min; MS m/z 274 (M', 69%), 259 (24), 243 (48), 228 (28), 217 (48), 211 (100), 197 (37), 185 (95), 165 (50), 153 (47), 139 (23), 121 (23), 115 (30), 105 (14), 89 (25), 77 (21), 45 (52).

Cis *and* trans-*3,6-dimethoxy-3-[4-(dimethoxymethyl)phenyl]-6-methylcyclohexa-1,4-diene* (**11**). Colourless oil (9% yield). *Cis* isomer t_r=12.48 min, *trans* isomer t_r=12.38 min; IR ν_{max} 3020, 2820, 1600, 1210, 1090, 1070, 810, 770 cm^{-1}; *cis* isomer ^1H NMR δ7.45 (m, 4H), 5.95 (s, 4H), 5.40 (s, 1H), 3.35 (s, 3H), 3.30 (s, 6H), 3.25 (s, 3H), 1.35 (s, 3H); *trans* isomer ^1H NMR δ 7.45 (m, 4H), 5.95 (s, 4H), 5.40 (s, 1H), 3.30 (s, 6H), 3.20 (s, 3H), 3.15 (s, 3H), 1.40 (s, 3H); MS m/z 304 (M', 68%), 289 (19), 273 (83), 258 (11), 247 (54), 241 (21), 227 (27), 215 (60), 211 (70), 195 (29), 165 (24), 153 (29), 151 (28), 129 (22), 115 (20), 75 (100). Anal. calc. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.97; H, 7.93.

Cis *and* trans-*6-ethyl-3,6-dimethoxy-3-phenylcyclohexa-1,4-diene* (**12**). Colourless oil (5% yield). *Cis* isomer t_r=7.94 min, *trans* isomer t_r=7.83 min; IR ν_{max} 3040, 2820, 1600, 1070, 750, 690, 670 cm^{-1}; *cis* isomer ^1H NMR δ7.30 (m, 5H), 5.90 (s, 4H), 3.30 (s, 3H), 3.20 (s, 3H), 2.00 (q, 2H, J=7 Hz), 0.95 (t, 3H, J=7 Hz); *trans* isomer ^1H NMR δ 7.30 (m, 5H), 5.90 (s, 4H), 3.20 (s, 3H), 3.05 (s, 3H), 2.00 (q, 2H, J=7 Hz), 0.95 (t, 3H, J=7 Hz); MS m/z 244 (M', 9%), 215 (100), 200 (45), 185 (22), 184 (19), 170 (12), 169 (17), 167 (20), 153 (18), 152 (24), 141 (30), 128 (16), 115 (44), 91 (10), 77 (35), 51 (19). Anal. calc. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.61; H, 8.28.

3-(4-Ethylphenyl)-3,6,6-trimethoxycyclohexa-1,4-diene (**13**). Colourless oil (4% yield). t_r=10.71 min; IR ν_{max} 3020, 2820, 1600, 1070, 750, 690, 670 cm^{-1}; ^1H NMR δ 7.40 (d, 2H, J=8 Hz), 7.10 (d, 2H, J=7 Hz), 6.05 (AB, 4H, J_{AB}=10 Hz, Δν=19 Hz), 3.40 (s, 3H), 3.35 (s, 3H), 3.30 (s, 3H), 2.60 (q, 2H, J=7 Hz), 1.25 (t,

3H, J=7 Hz); MS m/z 274 (M$^+$, 72%), 243 (100), 228 (63), 227 (29), 215 (13), 214 (18), 213 (15), 212 (35), 199 (70), 197 (66), 169 (23), 165 (16), 154 (37), 153 (30), 152 (30), 141 (20), 128 (26), 115 (34), 89 (11), 77 (20). Anal. calc. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.51; H, 8.02.

*3-(4-*tert*-butylphenyl)-3,6,6-trimethoxycyclohexa-1,4-diene* (**14**). t_r=13.68 min; MS m/z 302 (M$^+$, 100%), 287 (44), 271 (76), 255 (28), 240 (24), 231 (20), 227 (38), 225 (91), 215 (44), 211 (47), 200 (69), 199 (40), 197 (33), 183 (20), 171 (33), 165 (37), 153 (25), 152 (29), 141 (24), 139 (23), 128 (37), 115 (42), 114 (59), 99 (27), 91 (18), 77 (20), 57 (79).

*4-(4-*tert*-butylphenyl)-4-methoxycyclohexa-2,5-dienone* (**14a**). White solid. t_r=12.07 min; m.p. 102-103°C (methanol); IR ν_{max} 3040, 2820, 1660, 1630, 1600, 850, 830, 700 cm^{-1}; ^{1}H NMR δ 7.25 (s, 4H), 6.75 (AB, 4H, J_{AB}=10 Hz, $\Delta\nu$=28 Hz), 3.35 (s, 3H), 1.30 (s, 9H); MS m/z 256 (M$^+$, 53%), 241 (52), 228 (30), 226 (20), 225 (14), 213 (100), 211 (48), 210 (50), 199 (84), 185 (32), 182 (23), 171 (20), 165 (32), 157 (33), 152 (24), 141 (20), 139 (24), 128 (28), 115 (50), 91 (17), 77 (23), 57 (35). Anal. calc. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.62; H, 7.84.

4-(Methoxymethyl)biphenyl (**15**). t_r=8.23 min; MS m/z 198 (M$^+$, 82%), 167 (100), 152 (84), 128 (17), 115 (29), 89 (14), 77 (23), 63 (24), 51 (24).

4-(Dimethoxymethyl)biphenyl (**16**). Colourless oil (26% yield). t_r=9.25 min; IR ν_{max} 3060, 3020, 1600, 1190, 1100, 1050, 820, 760, 750, 690 cm^{-1}; ^{1}H NMR δ 7.50 (m, 9H), 5.45 (m, 1H), 3.35 (s, 6H); MS m/z 228 (M$^+$, 10%), 197 (100), 182 (11), 152 (19), 115 (15). Anal. calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.85; H, 6.99.

4-Phenylbenzaldehyde (**16a**). White solid. t_r=7.73 min; m.p. 59-60°C (hexane), (lit.,[15] m.p. 60°C); IR ν_{max} 3060, 1690, 1600, 760, 700 cm^{-1}; ^{1}H NMR δ 10.10 (s, 1H), 7.95 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz), 7.55 (m, 5H); MS m/z 182 (M$^+$, 93%), 181 (100), 153 (40), 152 (70), 127 (9), 119 (10), 117 (10), 76 (23), 51 (14).

4-(Trimethoxymethyl)biphenyl (**17**). t_r=9.94 min; MS m/z 258 (M$^+$, 6%), 227 (100), 212 (10), 181 (34), 153 (16), 105 (10), 76 (11).

Methyl 4-phenylbenzoate (**17a**). White solid. t_r=9.41 min; m.p. 116-117°C (hexane/ethyl acetate), (lit.,[16] m.p. 117-118°C); IR ν_{max} 3060, 1710, 1600, 1290, 1270, 1100, 860, 750 cm^{-1}; ^{1}H NMR δ 8.10 (d, 2H, J=8 Hz), 7.65 (d, 2H, J=8 Hz), 7.55 (m, 5H), 3.95 (s, 3H); MS m/z 212 (M$^+$, 65%), 181 (100), 153 (26), 152 (57), 127 (7), 75 (23).

4-Methoxymethyl-4'-methylbiphenyl (**18**). t_r=6.77 min; MS m/z 212 (M$^+$, 82%), 181 (100), 165 (46), 152 (30), 115 (21), 91 (14), 89 (14), 77 (12), 63 (18).

4-(Dimethoxymethyl)-4'-methylbiphenyl (**19**). t_r=8.88 min; MS m/z 242 (M$^+$, 15%), 211 (100), 165 (11), 152 (11), 115 (3).

4-(4-Methylphenyl)benzaldehyde (**19a**).[17] t_r=6.43 min; MS m/z 196 (M$^+$, 100), 195 (87), 167 (19), 165 (32), 152 (38), 115 (12).

4-Trimethoxymethyl-4'-methylbiphenyl (**20**). t_r=9.96 min; MS m/z 272 (M$^+$, 13%), 241 (100), 195 (15), 165 (10), 152 (8), 120 (5).

1-(4-Biphenylyl)-1-methoxyethane (**21**). Colourless oil (9% yield). t_r=7.66 min; IR ν_{max} 3040, 3020, 2820, 1600, 1100, 900, 840, 760, 730, 690 cm^{-1}; ^{1}H NMR δ 7.50 (m, 9H), 4.35 (q, 1H, J=7 Hz), 3.25 (s, 3H), 1.45 (d, 3H, J=7 Hz); MS m/z 212 (M$^+$, 18%), 197 (100), 181 (26), 178 (5), 165 (10), 152 (21). Anal. calc. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.92; H, 7.63.

1-(4-Biphenylyl)-1,1-dimethoxyethane (**22**). Colourless oil (21% yield). t_r=9,23 min; IR ν_{max} 3040, 3020, 2820,

1600, 1100, 1050, 840, 760, 750, 690 cm^{-1}; ^1H NMR δ 7.55 (m, 9H), 3.20 (s, 3H), 3.15 (s, 3H), 1.55 (s, 3H); MS m/z 242 (M^+, 6%), 227 (13), 211 (100), 210 (63), 209 (43), 181 (33), 180 (22), 179 (21), 178 (28), 167 (22), 165 (35), 151 (58), 133 (24), 115 (12), 89 (12), 77 (10), 43 (17). Anal. calc. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.25; H, 7.55.

1-(4-Biphenylyl)ethanone (**22a**).[18] White solid. t_r=8.92 min; m.p. 109-110°C (hexane); IR ν_{max} 3080, 1670, 1600, 910, 830, 760, 720, 690 cm^{-1}; ^1H NMR δ 8.05 (d, 2H, J=8 Hz), 7.65 (d, 2H, J=8 Hz), 7.55 (m, 5H), 2.65 (s, 3H); MS m/z 196 (M^+, 39%), 181 (91), 152 (100), 151 (36), 126 (20), 102 (13), 87 (10), 77 (14), 76 (15), 75 (17), 74 (18), 51 (21), 43 (36).

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References and Notes

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