

# The Electrochemical Methoxylation of Dialkoxyaromatic Compounds and the Determination of Isomer Ratios by N.M.R. Spectroscopy

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Electrolysis in methanol-KOH solution of *p*-diethoxy-, *p*-di-*n*-propoxy-, *p*-di-isopropoxy-, *p*-di-*n*-butoxy-, *p*-di-isobutoxy-, and *p*-di-*s*-butoxy-benzenes afforded the corresponding 3,6-dialkoxy-3,6-dimethoxycyclohexa-1,4-diene, shown by <sup>1</sup>H n.m.r. spectroscopy to be an approximately equimolar mixture of *cis*- and *trans*-isomers. Likewise, from 9,10-diethoxyanthracene was obtained an equimolar mixture of the *cis*- and *trans*-isomers of 9,10-diethoxy-9,10-dimethoxy-9,10-dihydroanthracene.

## Discussion

The electrochemical methoxylation of *o*-, *m*-, and *p*-dimethoxybenzene in methanol-KOH solution using a platinum anode has been previously described by Weinberg and Belleau.<sup>1</sup> From *p*-dimethoxybenzene one product only was obtained, identified as 3,3,6,6-tetramethoxycyclohexa-1,4-diene. Current/potential data and a Tafel plot corrected for background solvent oxidation suggested that the mechanism of reaction involved anodic oxidation of the aromatic compound to a radical cation, followed by reactions with methoxide ion and further electrochemical oxidation according to the Scheme. The same product was also obtained in good yield using vitreous and amorphous carbon anodes.

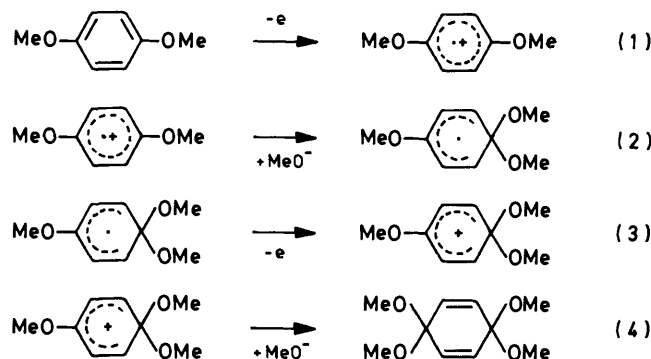
The stereochemical configuration of the tetramethoxycyclohexadiene was subsequently determined by *X*-ray crystallography<sup>2</sup> which showed the ring to be almost planar, the methoxy groups being situated above and below the plane of the ring.

The electrochemical methoxylation of other *p*-disubstituted aromatic ethers is of interest since this could give rise to mixtures of isomeric diacetals resulting from *cis* and *trans* addition of the two incoming methoxide groups. Determination of this isomer ratio might then provide information concerning the stereochemistry of the addition process.

The electrochemical oxidation of *p*-bis(2-hydroxyethoxy)-benzene in methanol-KOH solution has been investigated,<sup>3</sup> although in this case the tetra-alkoxycyclohexa-1,4-diene was not obtained owing to intramolecular cyclization leading to the formation of 8-(2-hydroxyethoxy)-8-methoxy-1,4-dioxaspiro[4.5]deca-6,9-diene.

We have investigated the methoxylation of some simple *p*-dialkoxybenzenes in methanol-KOH solution at a platinum anode in an undivided cell similarly to Weinberg and Belleau.<sup>1</sup> From the reaction with *p*-diethoxybenzene in methanol-KOH we isolated a good yield (77%) of 3,6-diethoxy-3,6-dimethoxycyclohexa-1,4-diene (1), identified by the usual techniques. The <sup>1</sup>H n.m.r. spectrum showed a triplet at  $\delta$  1.14 (*J* 7 Hz) due to CH<sub>3</sub>CH<sub>2</sub>O, a quartet at  $\delta$  3.48 (*J* 7 Hz), due to CH<sub>3</sub>CH<sub>2</sub>O and singlets at  $\delta$  3.20 and 5.92 ascribed to CH<sub>3</sub>O and the aryl protons, respectively. An alternative synthesis using *p*-dimethoxybenzene in ethanol-KOH failed, starting material being recovered almost quantitatively.

Similarly, from the anodic methoxylation of *p*-di-*n*-propoxy- and *p*-di-*n*-butoxy-benzene were isolated 3,6-di-*n*-propoxy- and 3,6-di-*n*-butoxy-3,6-dimethoxycyclohexa-1,4-diene, (2) and (3), both in good yield (72 and 90%, respectively), with consistent analyses and spectral properties. The structures of 3,6-diethoxy- and 3,6-di-*n*-propoxy-3,6-dimethoxycyclohexa-1,4-diene were further confirmed by partial hydrolysis to 4-ethoxy-4-methoxy- and 4-methoxy-4-*n*-propoxy-cyclohexa-2,5-dienone, (4) and (5) respectively, both identified in the



Scheme.

usual way. The hydrolysis was carried out using a dilute KH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> buffer solution since we found this to be more reliable than the previously reported methods.<sup>1,4</sup> Even so, we were unable to obtain a pure sample of the 4-*n*-butoxy-4-methoxydienone.

Compound (1), obtained after solvent evaporation of the product from the methoxylation of *p*-diethoxybenzene, was a solid, m.p. *ca.* room temperature, with a wide range indicating it to be a mixture of isomers. <sup>1</sup>H N.m.r. spectroscopy at low temperatures resulted in only a broadening of the existing signals and loss of fine structure with no further splitting. However, in the presence of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium [Eu(fod)<sub>3</sub>] or tris(2,2,2,6-tetramethylheptane-3,5-dionato)europium [Eu(thd)<sub>3</sub>] the proton signals were moved downfield, and each of the signals ascribed to the various types of proton were resolved into pairs. Within the pairs, the signals were of approximately equal intensity. The shifts were dependent on the ratio of shift reagent : diene (Tables 1 and 2). The fine structure in the proton signals was reduced owing to line broadening by the shift reagent, particularly at the higher concentrations.

The product from the electrolysis was recrystallized twice to afford a solid, m.p. 47–49 °C. The n.m.r. spectrum of this was identical with that of the unrecrystallized mixture, and analysed correctly for the diethoxydimethoxycyclohexa-1,4-diene (1). On addition of Eu(fod)<sub>3</sub> only one signal corresponding to each type of proton was observed at  $\delta$  4.68, 9.06, 12.16, and 17.18 [with correct intensity ratios for compound (1)]. Interpolation of the data in Table 1 at the ratio of Eu(fod)<sub>3</sub> : diene used gives estimated values for the shifts of  $\delta$  4.77, 9.05, 12.19, and 17.20 for the solid (isomer A). ( $\delta$  Values for isomer B would be predicted as 5.06, 8.85, 12.41, and 17.43.) A similar result was obtained using Eu(thd)<sub>3</sub> with the solid isomer, when only one series of absorptions was observed,

**Table 1.** Isomer proton shifts vs  $\text{Eu}(\text{fod})_3$ : diene ratio for 3,6-diethoxy-3,6-dimethoxycyclohexa-1,4-diene

Eu( $\text{fod}_3$ ) (mol $\times 10^5$ )	Mol ratio Eu( $\text{fod}_3$ ): diene	Chemical shifts ( $\delta$ values)			
		$\text{CH}_3\text{CH}_2\text{O}$	$\text{CH}_3\text{O}$	$\text{CH}_3\text{CH}_2\text{O}$	Vinylic H
0.00	0.000	1.141 (t, $J$ 7 Hz)	3.181 (s)	3.465 (q, $J$ 7 Hz)	5.878 (s)
2.89	0.507	2.662, 2.723	5.375, 5.435	6.893	10.465
5.79	1.016	3.871, 3.981	7.198, 7.243	9.715	14.266
8.66	1.519	4.520, 4.760	8.447, 8.596	11.538, 11.763	16.434, 16.533
10.00	1.754	4.685, 4.975	8.851, 9.011	12.088, 12.388	17.083, 17.183
11.94	2.095	4.995, 5.345	9.491, 9.730	13.037, 13.437	18.172, 18.322
14.28	2.505	5.195, 5.594	9.910, 10.190	13.716, 14.186	18.931, 19.051
Integration <sup>a</sup>		23.7	23.7	16.4	16.2
Total height		(3 H)	(3 H)	(2 H)	(2 H)
Individual peaks		11.9, 11.8	12.0, 11.7	8.1, 8.3	<i>b</i>

<sup>a</sup> For  $\text{Eu}(\text{fod})_3$ : diene = 2.505 : 1.00. <sup>b</sup> Absorptions insufficiently resolved for separate integration.

**Table 2.** Isomer proton shifts vs  $\text{Eu}(\text{thd})_3$ : diene ratio for 3,6-diethoxy-3,6-dimethoxycyclohexa-1,4-diene

Eu( $\text{thd}_3$ ) (mol $\times 10^5$ )	Mol ratio Eu( $\text{thd}_3$ ): diene	Chemical shifts ( $\delta$ values)			
		$\text{CH}_3\text{CH}_2\text{O}$	$\text{CH}_3\text{O}$	$\text{CH}_3\text{CH}_2\text{O}$	Vinylic H
0.00	0.00	1.141	3.181	3.465	5.878
3.50	0.65	3.147, 3.247	6.374, 6.494	8.621 <sup>a</sup>	12.468 <sup>a</sup>
4.63	0.86	3.746, 3.878	7.343, 7.493	10.220 <sup>a</sup>	14.515 <sup>a</sup>
7.51	1.40	5.095, 5.295	9.510, 9.900	13.656, 13.886	18.432 <sup>a</sup>
9.72	1.81	5.604, 5.944	10.450, 10.949	15.135, 15.524	19.960 <sup>a</sup>
12.68	2.36	5.744, 6.144	10.845, 11.389	15.784, 16.184	20.629 <sup>a</sup>
Integrations <sup>b</sup>					
Total height		29.3 (3 H)	28.8 (3 H)	18.4 (2 H)	18.7 (2 H)
Individual peaks		14.5, 14.8	14.6, 14.2	9.3, 9.1	

<sup>a</sup> No resolution observed. <sup>b</sup> For  $\text{Eu}(\text{thd})_3$ : diene = 1.81 : 1.00.

in the correct intensity ratio for compound (1) at  $\delta$  5.41, 10.55, 14.54, and 19.33: interpolation of the data in Table 2 gave estimated values of  $\delta$  5.41, 10.60, 14.71, and 19.49. ( $\delta$  Values predicted for isomer B are 5.70, 10.19, 14.98 and 19.50.) We therefore conclude that the recrystallized compound is essentially >95% pure single isomer A.

The mother-liquors from the recrystallization were evaporated to leave a liquid with an n.m.r. spectrum identical with that of the original isomer mixture [in the absence of  $\text{Eu}(\text{fod})_3$ ]. Addition of shift reagent caused the  $^1\text{H}$  n.m.r. signals to be split into pairs: integration showed the mixture to consist of the two isomers in the ratio A : B = 1 : 1.75.

From these spectra it is clear that the high-field signals of each pair due to  $\text{CH}_3\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{O}$ , and the vinylic protons and the low-field signal of the pair due to  $\text{CH}_3\text{O}$  arise from isomer A, and conversely for isomer B. These results were confirmed for the diethoxycyclohexadiene using  $\text{Eu}(\text{thd})_3$  as shift reagent (Table 2).

Similar results were obtained from the n.m.r. spectra of 3,6-dimethoxy-3,6-di-n-propoxy- and 3,6-di-n-butoxy-3,6-dimethoxy-cyclohexa-1,4-diene prepared by the electrolysis of *p*-di-n-propoxy- and *p*-di-n-butoxy-benzene. For these, n.m.r. spectroscopy in the presence of  $\text{Eu}(\text{fod})_3$  showed a duplication of the signals due to each type of proton, in the intensity ratio ca. 1 : 1, although in the case of the di-n-butoxy derivative the signal due to the  $\text{CH}_3(\text{CH}_2)_3\text{O}$  protons was obscured by  $\text{Eu}(\text{fod})_3$ . The electrolysis products from the last two examples were liquid and the isomers could therefore not be separated by fractional crystallization.

Also prepared from *p*-di-isopropoxybenzene was 3,6-di-isopropoxy-3,6-dimethoxycyclohexa-1,4-diene (6). The  $^1\text{H}$

n.m.r. spectrum showed absorptions at  $\delta$  1.11 and 5.89 due to the methyl groups and the vinylic protons, respectively, in the correct intensity ratios. At 60 MHz the signals at  $\delta$  3.18, due to the methoxy groups (with the correct total intensity ratio) was a doublet, separated by 1.2 Hz, and the signal at  $\delta$  3.7—4.2 arising from the tertiary proton was analysed as two heptets ( $J$  6.0 Hz) separated by 3 Hz. At 100 MHz the separation of the heptets increased to 4.5 Hz and with spin-decoupling the complex signal collapsed to two lines, again separated by 4.5 Hz, confirming the presence of two isomeric compounds, shown by integration to be in the ratio 1.20 : 1. The same ratio was also obtained by integration of the signals due to the methoxy groups from spectra run in the presence of  $\text{Eu}(\text{fod})_3$ , the largest signal having the greatest chemical shift.

The  $^1\text{H}$  n.m.r. spectrum of 3,6-di-*s*-butoxy-3,6-dimethoxycyclohexa-1,4-diene (8) showed similar characteristics, with signals at  $\delta$  0.85, 1.1, 1.36, and 5.85 arising from the methyl, methylene, and vinylic protons, respectively, in the correct intensity ratios of 3 : 3 : 2 : 2, respectively, with the expected coupling ( $J$  6 Hz). The signal due to the tertiary proton at  $\delta$  3.73 was complex and could not be analysed. However, the methoxide proton signal at  $\delta$  3.18 consisted of two singlets separated by 1.4 Hz (*vide* the isopropoxy derivative where the separation was 1.2 Hz); at 100 MHz the separation increased to 2.5 Hz, indicating the presence of two isomeric compounds, which were shown by integration to be in the ratio 1.18 : 1, the largest signal having the greatest chemical shift. Attempts to confirm this ratio using  $\text{Eu}(\text{fod})_3$  were only partially successful owing to overlap of the peaks, but an isomer ratio of 1.17 : 1 was obtained by integration of the signals from the protons in the 4-position.

The  $^1\text{H}$  n.m.r. spectrum of 3,6-di-isobutoxy-3,6-dimethoxy-cyclohexa-1,4-diene (7) at both 60 and 100 MHz was correct for the named compound and showed signals at  $\delta$  0.90 ( $\text{CH}_3$ ), 1.76 (tert-H), 3.14—3.20 ( $\text{CH}_3\text{O}$  and  $-\text{CH}_2\text{O}$ ), and 5.89 (vinyl H) in the correct intensity ratios: no splitting of the methylene protons or the methoxy protons was observed. In the presence of  $\text{Eu}(\text{fod})_3$ , the signals due to the various protons were duplicated and although some overlap occurred, the pair of signals due to the methylene protons adjacent to oxygen were distinct. Integration of these suggested an isomer ratio of 1.04 : 1, the greater signal having the smaller chemical shift.

Finally, 9,10-diethoxy-9,10-dimethoxy-9,10-dihydroanthracene (9) was prepared by the electrochemical methoxylation of 9,10-diethoxyanthracene. The product of the electrolysis had a correct elemental analysis, top mass peak, and the  $^1\text{H}$  n.m.r. spectrum (at 60 MHz) was consistent with the assigned structure. In the presence of  $\text{Eu}(\text{fod})_3$ , the signals due to the methyl and methoxide protons were resolved into pairs, shown by integration to be of approximately equal intensity. Resolution of the methylene protons was not observed.

The m.p. of the anthracene derivative also suggested that the product consisted of a mixture of isomers. The product as originally prepared showed a wide melting range (115—145 °C) and recrystallization of the mixture three times from benzene gave a small yield (30%) of solid, m.p. 171—173 °C, shown by thin layer chromatography to be a single component.

There have been a number of investigations of the electrochemical addition of methoxy-,<sup>6-11,16</sup> acetoxy-,<sup>12-14</sup> and benzyloxy-<sup>15</sup> groups to alkenes and aromatic compounds, and discussions of the influence of the electrode on the stereochemistry of the products. However, the products from the electrochemical addition of acetoxy- and benzyloxy-groups have been explained in terms of the formation of acetyloxonium and benzyloxonium cyclic intermediates so that the relevance of the results to electrode control of the stereochemistry of the reactions is doubtful. Anodic methoxylation reactions appear to be free from these mechanistic complexities and the addition of methoxide ion to a variety of substrates has afforded mixtures of isomeric dimethoxy adducts which have indicated, in some cases, the preferential formation of one of the isomers.

It is generally accepted that these anodic reactions proceed via an ECEC (Scheme) mechanism terminating with the addition of a second methoxide ion to a cation (step 4 in Scheme). However, it has been shown<sup>13</sup> that during the acetoxylation of 1,2-bis(4-methoxyphenyl)ethene one-electron oxidation occurs at low potentials and that this gives rise to dimeric products, whereas the anticipated simple addition product is formed only at high potentials, where the initial step is a two-electron transfer. This has been ascribed to rapid dimerization of the cation radical formed at low potentials before reaction with acetate could occur. Dimerization has not been observed during anodic methoxylation, possibly owing to the greater nucleophilicity of the methoxide ion leading to more rapid addition.

If the first step in the electrochemical oxidation is adsorption of the substrate with the plane of the aromatic ring parallel to the electrode (as is generally assumed), followed by loss of an electron, addition of the first methoxide ion to the cation radical would have to take place on the side of the molecule away from the electrode. This would be followed by a second electron transfer, and provided the cation remained adsorbed onto, or was close to, the electrode the second methoxide ion would add to the same side of the molecule resulting in *cis* addition. If the final cation is rapidly desorbed from the electrode owing to loss of aromaticity and/or

electrostatic repulsion, then *trans* addition becomes possible. The extent of this may then depend on the stability of the cation.

The formation of an excess of the *cis*-dimethoxy adduct from *cis*- and *trans*-stilbene has been observed<sup>9-11</sup> possibly because the aromaticity of the substrate has not been substantially diminished and adsorption may still be strong. Methoxylation of 2,5-dimethylfuran<sup>6,7</sup> shows an equal extent of *cis* and *trans* addition of two methoxy groups to the 2,5-positions, and in this case adsorption of the cation intermediate may well be less strong than for that obtained from stilbene. In addition, mesomeric stabilization of the cation by the oxygen atom  $\alpha$  to the cationic centre would be greater than that due to the phenyl group in the stilbene intermediate (Hammett  $\sigma_p$ :  $\text{OMe}$ ,  $-0.27$ ;  $\text{C}_6\text{H}_5$ ,  $+0.01$ ).<sup>17</sup> These results are in agreement with results obtained from the methoxylation of 9,10-diethyl-, 9,10-dipropyl-, and 9,10-diphenylanthracene where a 1 : 1 ratio of *cis* : *trans* adducts was found.<sup>16</sup> In these latter examples, although strong adsorption could be expected, the cation is known<sup>18</sup> to be very stable so that diffusion from the anode would enable the incoming methoxide group to approach freely from each side of the cation centre. An anomalous result for methoxide addition to anthracene and 9,10-dimethylanthracene has been reported<sup>8</sup> in that the ratio of *cis* : *trans* addition of 71 : 29 and 83 : 17, respectively, has been claimed (although reported as the reverse in ref. 16). Our preliminary experiments with anthracene using the method described<sup>8</sup> suggest a *cis* : *trans* isomer ratio of 1.2 : 1 (by integration of the n.m.r. absorptions due to both the benzylic and methoxy protons), although the product contained components other than the expected dimethoxy adduct and unchanged anthracene.

The result we obtained for the methoxylation of *p*-diethoxybenzene indicates an isomer ratio of close to unity, suggesting no appreciable influence of the electrode surface. This may well be due, on our hypothesis, to rapid desorption of the cation intermediate (following loss of aromaticity) which, as a result of mesomeric stabilization by the alkoxide group attached to the cationic centre, is sufficiently stable to diffuse away from the electrode, so making addition of a second methoxide ion to either side of the ring equally possible. For *p*-di-*n*-propoxy- and *p*-di-isobutoxy-benzene, the ratio of isomers is only slightly greater than unity, although for *p*-di-isopropoxy- and *p*-di-*s*-butoxy-benzene it increases to ca. 1.2 : 1.

It is of interest that in the presence of complexing agent the methoxy signals are shifted uniformly less than the protons  $\alpha$  to oxygen in the other alkoxy groups. In addition, the more abundant isomer has the smallest shift of the two methoxy signals and the greatest shift for the protons  $\alpha$  to oxygen in the alkoxy groups. This suggests that in all our examples the isomer in excess has the same stereochemistry, although we are unable to assign the configuration from the n.m.r. data. However, the isomer ratio increases with increasing size and extent of branching at the  $\alpha$ -position of the alkoxy group in the order ethoxy- (1 : 1) < isobutoxy- (1 : 1.04), *n*-propoxy- (1 : 1.08) < *s*-butoxy- (1.18), isopropoxy- (1 : 1.20). From this we suggest that the isomer in excess is the *trans*-isomer, the approach of the incoming methoxide group being more sterically hindered for *cis* addition.

## Experimental

**Apparatus.**—I.r. spectra were recorded using a Perkin-Elmer 257 spectrophotometer and u.v. spectra (in ethanol) on a Pye-Unicam SP800 spectrometer.  $^1\text{H}$  N.m.r. spectra (in  $\text{CCl}_4$ ) were recorded on Perkin-Elmer R-14 (100 MHz) or R-12B (60 MHz) spectrometers.

The alkoxybenzenes were prepared from the corresponding alkyl halide and hydroquinone by a Williamson synthesis using potassium carbonate or the sodium salt of the phenol in alcohol and have been previously described in the literature.<sup>19</sup> All had a correct chemical analysis, top mass peak, and <sup>1</sup>H n.m.r. spectrum.

9,10-Diethoxyanthracene was prepared according to the method described.<sup>5</sup> Ether refers to diethyl ether.

**General Procedure.**—Electrolyses were carried out in an undivided glass cell cooled in ice, fitted with a magnetic stirrer, a cylindrical platinum anode (5 × 8 cm), and nickel cathode. The dialkoxyaromatic was dissolved in methanol (140 cm<sup>3</sup>) containing KOH (1.5 g) and electrolysed at constant current. At the end of the electrolysis the electrolyte was evaporated to a small bulk under reduced pressure at room temperature, water (250 cm<sup>3</sup>) was added and the solution extracted with ether (3 × 50 cm<sup>3</sup>). The ether extracts were dried (MgSO<sub>4</sub>) and evaporated to afford the product. For the determination of isomer ratios the <sup>1</sup>H n.m.r. spectrum of this product was recorded before any further treatment.

**3,6-Diethoxy-3,6-dimethoxycyclohexa-1,4-diene** (1). Electrolysis of *p*-diethoxybenzene (15.0 g) for 5 h at 2.5 A and work-up as described above afforded a mixture of the isomers of **3,6-diethoxy-3,6-dimethoxycyclohexa-1,4-diene** (1) (15.8 g) (Found: C, 63.5; H, 8.6. C<sub>14</sub>H<sub>20</sub>O<sub>4</sub> requires C, 63.1; H, 8.8%); *M*<sup>+</sup> 228 (required); λ<sub>max.</sub> 207.5 nm (ε<sub>max.</sub> 1 640); ν<sub>max.</sub> 2 960 (aliph. CH), 1 450, 1 400, 1 310, 1 200—1 000, 970, and 900 cm<sup>-1</sup>; δ 1.14 (3 H, t, *J* 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 3.20 (3 H, s, CH<sub>3</sub>O), 3.47 (2 H, q, *J* 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>O), and 5.90 (2 H, s, vinylic H).

**3,6-Dimethoxy-3,6-di-*n*-propoxycyclohexa-1,4-diene** (2). Electrolysis of *p*-di-*n*-propoxybenzene (2.88 g) for 2 h at 2.5 A, followed by the usual work-up, gave a mixture of the isomers of **3,6-dimethoxy-3,6-di-*n*-propoxycyclohexa-1,4-diene** (2) (2.72 g) (Found: C, 65.7; H, 9.1. C<sub>14</sub>H<sub>24</sub>O<sub>4</sub> requires C, 65.6; H, 9.4%); *M*<sup>+</sup> 256 (required); λ<sub>max.</sub> 207.5 nm (ε<sub>max.</sub> 3 032); ν<sub>max.</sub> 2 960 (aliph. CH), 1 510, 1 460, 1 405, 1 310, 1 200—1 000, 960, and 900 cm<sup>-1</sup>; δ 0.91 (3 H, t, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.46 (2 H, sext, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 3.19 (3 H, s, CH<sub>3</sub>O), 3.35 (2 H, t, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), and 5.9 (2 H, s, vinylic H).

**3,6-Dimethoxy-3,6-di-*n*-butoxycyclohexa-1,4-diene** (3). Electrolysis of *p*-di-*n*-butoxybenzene (2.5 g) at 2.5 A for 2 h afforded, after the usual work-up, a mixture of the isomers of **3,6-dimethoxy-3,6-di-*n*-butoxycyclohexa-1,4-diene** (3) (2.87 g) (Found: C, 67.9; H, 10.2. C<sub>16</sub>H<sub>28</sub>O<sub>4</sub> requires C, 67.6; H, 9.9%); *M*<sup>+</sup> 284 (required); λ<sub>max.</sub> 205.5 nm (ε<sub>max.</sub> 1 983); ν<sub>max.</sub> 2 960 (aliph. CH), 1 460, 1 405, 1 310, 1 190, 1 105, 1 065, 1 035, and 970 cm<sup>-1</sup>; δ 0.90 [3 H, distorted t, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>O], 1.4 [4 H, m, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>O], 3.18 (3 H, s, CH<sub>3</sub>O), 3.40 [2 H, t, *J* 7 Hz, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>O], and 5.89 (2 H, s, vinylic H).

**3,6-Di-isopropoxy-3,6-dimethoxycyclohexa-1,4-diene** (6). Electrolysis of *p*-di-isopropoxybenzene (2.0 g) at 2.5 A for 1.5 h afforded **3,6-di-isopropoxy-3,6-dimethoxycyclohexa-1,4-diene** (6) (2.25 g) (Found: C, 65.4; H, 9.7. C<sub>14</sub>H<sub>24</sub>O<sub>4</sub> requires C, 65.6; H, 9.4%); *M*<sup>+</sup> 256 (required); λ<sub>max.</sub> 207.5 nm (ε<sub>max.</sub> 3 032); ν<sub>max.</sub> 2 960 (aliphatic CH), 1 460, 1 400, 1 375, 1 361, 1 310, 1 174, 1 094, 1 060, 1 025, 987, and 939; δ 1.11 [6 H, d, *J* 6.0 Hz (CH<sub>3</sub>)<sub>2</sub>CHO], 3.18 (3 H, two signals, separation 1.2 Hz, CH<sub>3</sub>O), 4.00 and 4.03 [1 H, 2 hept., separated by 3 Hz, *J* 6.0 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-O], and 5.89 (2 H, s, vinylic H).

**3,6-Di-isobutoxy-3,6-dimethoxycyclohexa-1,4-diene** (7). Electrolysis of 1,4-di-isobutoxybenzene (1 g) at 2 A for 2 h afforded **3,6-di-isobutoxy-3,6-dimethoxycyclohexa-1,4-diene** (7) (0.4 g) (Found: C, 67.8; H, 9.7. C<sub>16</sub>H<sub>28</sub>O<sub>4</sub> requires C, 67.6; H, 9.9%); *M*<sup>+</sup> 253 (*M* - CH<sub>3</sub>O); ν<sub>max.</sub> 3 040, 2 920, 2 860 and 2 821 (aliphatic CH), 1 500, 1 455, 1 400, 1 360, 1 307, 1 221, 1 183, 1 100, 1 031, 970, and 900; δ 0.89 [6 H, d, *J* 7 Hz, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>O], 1.76 [1 H, m, *J* 7 Hz (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>O],

3.12—3.20 (5 H, m, CH<sub>3</sub>O and CH<sub>2</sub>O), and 5.89 (2 H, s, vinylic H).

**3,6-Dimethoxy-3,6-di-*s*-butoxycyclohexa-1,4-diene** (8). Electrolysis of *p*-di-*s*-butoxybenzene (2.0 g) at 2 A for 1.5 h afforded the title compound (8) (1.90 g) (Found: C, 67.3; H, 10.0. C<sub>16</sub>H<sub>28</sub>O<sub>4</sub> requires C, 67.6; H, 9.9%); *M*<sup>+</sup> 253 (*M* - CH<sub>3</sub>O); ν<sub>max.</sub> 3 040, 2 960, 2 925, 2 872, 2 825 (aliphatic CH), 1 640, 1 496, 1 455, 1 398, 1 369, 1 305, 1 185, 1 168, 1 100, 1 062, 1 030, 1 000, 963, 916, and 800; δ 0.85 [3 H, t, *J* 6 Hz, CH<sub>3</sub>CH<sub>2</sub>CH(Me)O], 1.1 [3 H, d, *J* 6 Hz CH<sub>3</sub>CH(Et)O], 1.36 [2 H, quin, *J* 6 Hz, CH<sub>3</sub>CH<sub>2</sub>CH(Me)O], 3.18 (3 H, two signals separated by 1.4 Hz, CH<sub>3</sub>O), 3.73 [1 H, m, CH<sub>3</sub>CH<sub>2</sub>-CH(Me)O], and 5.85 (2 H, s, vinylic H).

**9,10-Diethoxy-9,10-dimethoxy-9,10-dihydroanthracene** (9). 9,10-Diethoxyanthracene (1.2 g) was electrolysed at 2.5 A for 2 h to afford a white solid identified as **9,10-diethoxy-9,10-dimethoxy-9,10-dihydroanthracene** (9) (1.36 g) (Found: C, 73.1; H, 7.4. C<sub>20</sub>H<sub>24</sub>O<sub>4</sub> requires C, 73.2; H, 7.3%); *M*<sup>+</sup> 297 (*M* - OCH<sub>3</sub>); δ (100 MHz) 1.04 (6 H, t, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.88 (s, CH<sub>3</sub>O), and 3.03 (quart., *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>O, totalling 10 H), and 7.58 (8 H, m, aromatic H).

**4-Ethoxy-4-methoxycyclohexa-2,5-dienone** (4). A portion (28 cm<sup>3</sup>) of an aqueous buffer solution 0.025M with respect to KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> was diluted with water to 250 cm<sup>3</sup> and to this was added 3,6-diethoxy-3,6-dimethoxycyclohexa-1,4-diene (1.02 g). The mixture was stirred for 48 h at room temperature until homogeneous and then extracted with ether (3 × 50 cm<sup>3</sup>) to give a liquid residue (0.7 g), a portion (0.52 g) of which was distilled in vacuum (0.1 mmHg) to give **4-ethoxy-4-methoxycyclohexa-2,5-dienone** (4) (0.28 g), b.p. 221—222 °C (Found: C, 64.2; H, 7.2. C<sub>9</sub>H<sub>12</sub>O<sub>3</sub> requires C, 64.3; H, 7.2%); λ<sub>max.</sub> 217.5 nm (ε<sub>max.</sub> 14 111); ν<sub>max.</sub> 2 970, 2 930, 2 890, 2 820 (aliph. CH), 1 680, 1 670, 1 630 (C=C and C=O), 1 455, 1 440, 1 380, 1 310, 1 300, 1 175, 1 105—1 000, 975, 920, 895, and 855 cm<sup>-1</sup>; δ 1.19 (3 H, t, *J* 6.6 Hz, CH<sub>3</sub>-CH<sub>2</sub>O), 3.30 (3 H, s, CH<sub>3</sub>O), 3.59 (2 H, q, *J* 6.6 Hz, CH<sub>3</sub>CH<sub>2</sub>O), and an AB system *J*<sub>AB</sub> 10.5 Hz, δ<sub>A</sub> 6.72, δ<sub>B</sub> 6.14 (4 H, vinylic H).

**4-Methoxy-4-*n*-propoxycyclohexa-2,5-dienone** (5). To the buffer solution (50 cm<sup>3</sup>) was added water (400 cm<sup>3</sup>) and 3,6-dimethoxy-3,6-di-*n*-propoxycyclohexa-1,4-diene (2.0 g) and the mixture stirred for 5 days at room temperature. The aqueous solution was decanted from traces of uncharged starting material and extracted with ether. The extracts were dried (MgSO<sub>4</sub>) and evaporated to give a liquid residue (1.14 g), a portion (0.6 g) of which was distilled in vacuum (0.1 mmHg) to give **4-methoxy-4-*n*-propoxycyclohexa-2,5-dienone** (5) (0.26 g) (Found: C, 65.9; H, 8.0. C<sub>10</sub>H<sub>14</sub>O<sub>3</sub> requires C, 65.9; H, 7.8%); ν<sub>max.</sub> 2 950, 2 925, 2 865, 2 820 (aliph. CH), 1 680, 1 670, 1 630, 1 610 (C=C and C=O), 1 455, 1 380, 1 310, 1 300, 1 175, 1 105—1 000, 975, 915, and 855 cm<sup>-1</sup>; δ 0.95 (3 H, t, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.57 (2 H, sext, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 3.32 (3 H, s, CH<sub>3</sub>O), 3.47 (2 H, t, *J* 7 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), and an AB system *J*<sub>AB</sub> 10.8 Hz, δ<sub>A</sub> 6.69 and δ<sub>B</sub> 6.11.

**Isomer Ratio.**—(a) **3,6-Diethoxy-3,6-dimethoxycyclohexa-1,4-diene** (1). The <sup>1</sup>H n.m.r. spectrum of the title compound (1) (5.70 × 10<sup>-5</sup> mol) in CCl<sub>4</sub> (0.55 cm<sup>3</sup>) was recorded in the presence of Eu(fod)<sub>3</sub> [up to 2.5 mol of Eu(fod)<sub>3</sub> per mole of diene]. The signals showed a large shift, with loss of fine structures; each signal was resolved into a pair of signals, and Table 1 gives the shifts at various Eu(fod)<sub>3</sub>: diene ratios. Integration of the signals showed the isomer ratio to be ca. 1:1. A similar result was obtained when Eu(thd)<sub>3</sub> was used as shift reagent (Table 2).

The mixture of isomers (2.93 g) was separated by fractional crystallization three times from light petroleum (b.p. 40—60 °C) at 2 °C to afford a solid (0.42 g), m.p. 47—49 °C, with a

**Table 3.** Isomer proton shifts at  $\text{Eu}(\text{fod})_3$ : diene = 1.203:1 for 3,6-dimethoxy-3,6-di-n-propoxycyclohexa-1,4-diene

$\delta$	Assignment and coupling	Integration
1.278	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ (t, $J$ 7.2 Hz)	62
1.669	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ (t, $J$ 7.2 Hz)	57
3.666	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ (sext, $J$ 7.2 Hz)	41
4.093	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ (sext, $J$ 7.2 Hz)	38
6.244	$\text{CH}_3\text{O}$ (s)	} Total 118 <sup>a</sup>
6.293	$\text{CH}_3\text{O}$ (s)	
9.690	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ (m) <sup>b</sup>	39
10.290	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$ (m) <sup>b</sup>	37
14.316	Vinyl H (s)	38
14.805	Vinyl H (s)	35

<sup>a</sup> Signals not sufficiently resolved for separate integration. <sup>b</sup> Coupling not observable owing to line broadening by the shift reagent.

<sup>1</sup>H n.m.r. spectrum identical with that of the original liquid mixture. In the presence of  $\text{Eu}(\text{fod})_3$  ( $9.639 \times 10^{-5}$  mol) in  $0.55 \text{ cm}^3$   $\text{CCl}_4$  containing  $5.526 \times 10^{-5}$  mol diene) the <sup>1</sup>H n.m.r. spectrum showed only four signals, at  $\delta$  4.68, 9.06, 12.16, and 17.18.

The spectrum of the recrystallized diene ( $5.175 \times 10^{-5}$  mol) in the presence of  $\text{Eu}(\text{thd})_3$  ( $8.578 \times 10^{-5}$  mol) in  $\text{CCl}_4$  ( $0.50 \text{ cm}^3$ ) likewise showed four signals only, at  $\delta$  5.41, 10.55, 14.54, and 19.33.

The mother-liquors from the recrystallization were evaporated to give a liquid residue: <sup>1</sup>H n.m.r. spectroscopy in the presence of  $\text{Eu}(\text{fod})_3$  showed peaks at  $\delta$  4.83, 9.38, 12.57, and 17.59 ascribed to isomer A (the intensity ratios of these were 3:3:2:2) and at  $\delta$  5.15, 9.15, 12.92, and 17.73 ascribed to isomer B (the intensity ratio of these were also 3:3:2:2). The integration showed that the ratio of isomers A:B was 1:1.75.

(b) 3,6-Dimethoxy-3,6-di-n-propoxycyclohexa-1,4-diene (2). The <sup>1</sup>H n.m.r. spectrum of the diene ( $4.062 \times 10^{-5}$  mol) in  $\text{CCl}_4$  ( $0.55 \text{ cm}^3$ ) was taken in the presence of  $\text{Eu}(\text{fod})_3$  ( $4.887 \times 10^{-5}$  mol). Table 3 lists the signals observed and the intensity ratios, which indicate an isomer ratio of 1:1.08.

(c) Other dienes. The <sup>1</sup>H n.m.r. spectra of di-isopropoxy-, di-isobutoxy- and di-s-butoxy-dimethoxycyclohexa-1,4-diene, (6), (7), and (8), respectively, were also taken in the presence of  $\text{Eu}(\text{fod})_3$ . A sample of the diene (6) ( $1.328 \times 10^{-4}$  mol) in  $\text{CCl}_4$  ( $0.55 \text{ cm}^3$ ) containing  $\text{Eu}(\text{fod})_3$  ( $9.662 \times 10^{-5}$  mol) gave signals at  $\delta$  4.12 and 4.45 [both d,  $J$  5 Hz,  $(\text{CH}_3)_2\text{CHO}$ ], 5.00 and 5.16 (both s,  $\text{CH}_3\text{O}$ ), 9.30 [br,  $(\text{CH}_3)_2\text{CHO}$ ], and 11.84 and 11.93 (s, vinylic H). Integration of the methoxy signals gave a ratio of 1.20:1 (the downfield signal being the greater).

The <sup>1</sup>H n.m.r. spectrum of a solution of the di-isobutoxy-diene (7) ( $6.549 \times 10^{-5}$  mol) and  $\text{Eu}(\text{fod})_3$  ( $9.499 \times 10^{-5}$  mol) in  $\text{CCl}_4$  ( $0.55 \text{ cm}^3$ ) was not fully resolved, the signals due to the tertiary proton overlapping with those due to the methoxide group. Sharp signals due to  $\text{CH}_2\text{O}$  were observed at  $\delta$  11.10 and 11.96: integration of these gave an isomer ratio of 1:1.04.

From the <sup>1</sup>H n.m.r. spectrum of dimethoxy-di-s-butoxy-cyclohexadiene (8) ( $6.444 \times 10^{-5}$  mol) with  $\text{Eu}(\text{fod})_3$  ( $9.901 \times 10^{-5}$  mol) in  $\text{CCl}_4$  ( $0.55 \text{ cm}^3$ ), only the signal due to the methyl group attached to the methylene group was completely resolved, showing two triplets at  $\delta$  3.43 and 4.13; integration of these gave an isomer ratio of 1.17:1, the downfield signal having the greatest intensity.

The <sup>1</sup>H n.m.r. spectrum of 9,10-diethoxy-9,10-dimethoxy-9,10-dihydroanthracene (9) ( $6.86 \times 10^{-5}$  mol) with  $\text{Eu}(\text{fod})_3$  ( $9.74 \times 10^{-5}$  mol) in  $\text{CCl}_4$  ( $0.55 \text{ cm}^3$ ) showed signals at  $\delta$  2.90 and 3.25 ( $\text{CH}_3$ , t), 8.25 ( $\text{CH}_2\text{O}$ ), 9.25 and 9.60 ( $\text{CH}_3\text{O}$ , s) and a complex signal at 13.15–14.25 (aromatic H). The total intensity ratios of the signals were correct for the named compound. Integration of the signals due to the methyl protons and those due to methoxide suggested an isomer ratio of 1:1.

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