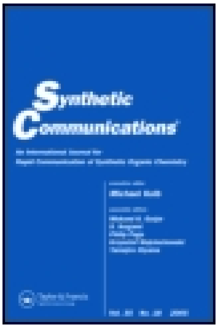

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# An Efficient, Simple and Inexpensive Method for the Preparation of 1,4-Benzoquinone Monoketals via Anodic Oxidation of 1,4-Dimethoxybenzenes

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SYNTHETIC COMMUNICATIONS, 24(20), 2989-3008 (1994)

# AN EFFICIENT, SIMPLE AND INEXPENSIVE METHOD FOR THE PREPARATION OF 1,4-BENZOQUINONE MONOKETALS *VIA* ANODIC OXIDATION OF 1,4-DIMETHOXYBENZENES

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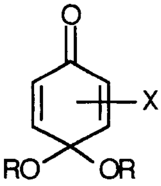
**Abstract**: Anodic oxidation of a series of 1-substituted-2,5-dimethoxybenzenes gives 2-substituted-1,1,4,4-tetramethoxycyclohexa-2,5-dienes in almost quantitative crude yield. Selective monohydrolysis of these bis-ketals is possible in many cases, and gives 3-substituted-4,4-dimethoxycyclohexa-2,5-dienones in good to excellent overall yield.

1,4-Benzoquinone monoketals (4,4-dialkoxycyclohexa-2,5-dienones) **1** are valuable polyfunctional molecules for synthesis. They have been extensively



**1**

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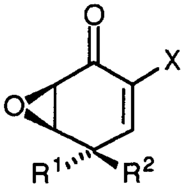
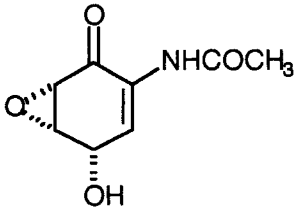
employed for a wide range of transformations[1-9] and are particularly attractive starting materials for the synthesis of polyoxygenated cyclohexane-based natural products. In this latter context, we have been interested for some time in the development of general methods for the preparation of biologically active, naturally occurring epoxides of the types **2** - **4**, and required ready access to a range of substituted 1,4-benzoquinone monoketals **1**.

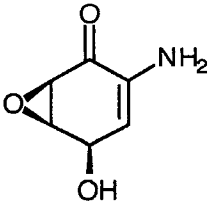
The most widely used general methods for the preparation of ketals **1** are based on chemical[9,10] or electrochemical[1,2,17-24] oxidation of phenols, 4-alkoxyphenols or 1,4-dialkoxyarenes, and good to excellent yields can often be obtained. The major disadvantages of metal salt based oxidations are the variable yields often encountered, overoxidation of products, and the incompatibility of sensitive functionality with the reagent and/or reaction conditions. Electrochemical



**2a**, $R^1 = H$; $R^2 = OH$; $X = CH_2OH$[11]
**b**, $R^1 = OH$; $R^2 = H$; $X = CH_3$[12]
**c**, $R^1 = OH$; $R^2 = H$; $X = OCH_3$[13,14]
**d**, $R^1 = OCOCH_3$; $R^2 = H$; $X = Br$[15]

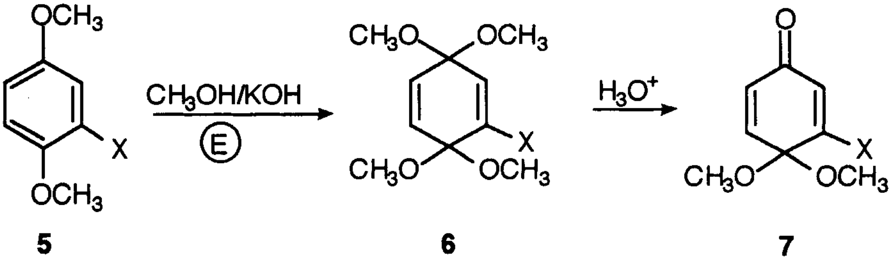


**3**[16]



**4**[16]

oxidation of 1,4-dialkoxyarenes **5** to 1,4-benzoquinone bis-ketals **6** followed by selective monohydrolysis (Scheme 1), by contrast, is a mild, simple and potentially versatile route to the 3-substituted monoketals **7**, as the major problems associated with metal salt oxidations can usually be circumvented by careful control of the reaction conditions.



Scheme 1

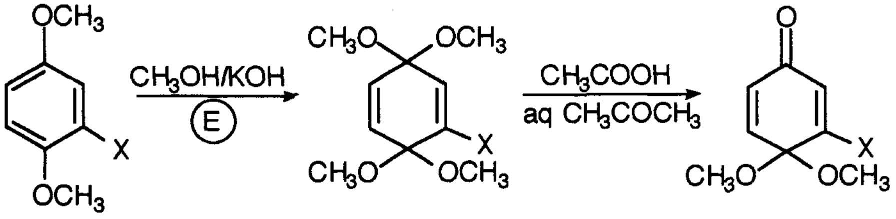
Expensive and sophisticated specialist electrochemical equipment which can be used for the transformation **5** → **6** is commercially available. We were intrigued, however, by the very simple and inexpensive apparatus for anodic oxidation described by Azadi-Ardakani and Wallace,[25] and used by them for the variable scale oxidation of **5** (X = H) to **6** (X = H) in 68-78% yield. We have exploited this procedure to explore the scope and limitations of the method for the preparation of a range of ketals **7** of interest to us for other work, and now summarise our results.

The apparatus used was essentially that described by Azadi-Ardakani and Wallace: a platinised titanium anode and two bridged nickel cathode plates. The electrodes were connected to a DC supply, a conventional car battery charger set at 5 volts. Oxidations were carried out at room temperature with currents ranging from 0.5 to 2 amps in a beaker open to the air, using 2% methanolic potassium hydroxide solution as both solvent and electrolyte; the level of dilution did not affect the results. Losses of solvent by evaporation were made up by addition of methanol as necessary. Traces of water in the electrolyte did not affect the results, and no control of electrode potential, temperature or current appeared to be necessary.

Oxidation of a variety of monosubstituted 1,4-dimethoxyarenes **5** proceeded smoothly and rapidly (< 3h) and the results are listed in the Table. Electrolyses were carried out on scales ranging from 1.5 to 250 mmol and yields were reproducible irrespective of scale. The 2-substituted-1,4-benzoquinone bis-ketals **6** were formed in excellent yields. In most cases the $^1$H nmr spectra showed only traces of impurities to be present in the crude product, and the data were fully consistent with the assigned structures. Treatment of the bis-ketals **6** with a 2% aqueous acetic acid solution in acetone at 0°C then at room temperature resulted in clean, rapid and selective acid catalysed monohydrolysis to the monoketals **7**. The yield in the case of the hydroxymethyl substituted product (**7**, X = $CH_2OH$) was only moderate, primarily because the product was very sensitive to air oxidation. Use of the silyl-protected alcohol **5**, (X = $CH_2OTBDMS$) gave only a marginal increase in yield, and hydrolysis of the bis-ketal (**6**, X = $CH_2OTBDMS$) proceeded with some simultaneous loss of the protecting group. The yield in the case of the acetamido derivative (**5**, X = $NHCOCH_3$) was also modest, but significantly greater than when anodic oxidation was carried out in a three compartment cell.[18]

Attempts to extend the method directly to 2,5-dimethoxybenzaldehyde, 2,5-dimethoxyacetophenone and 2,5-dimethoxybenzoic acid were unsuccessful. Anodic oxidation resulted in decomposition and gave complex mixtures of

**Table.** Anodic oxidation of monosubstituted 1,4-dimethoxyarenes **5**: preparation of monoketals **7** via bis-ketals **6**

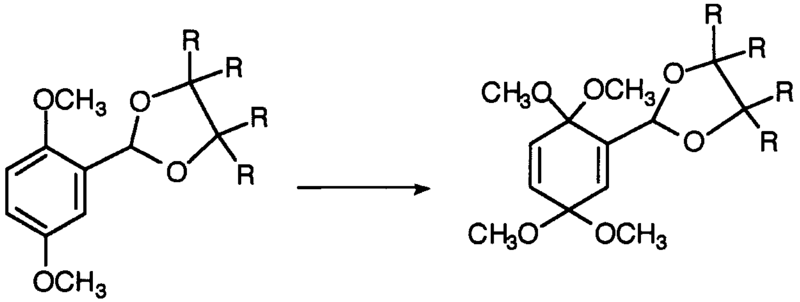


**5** **6** **7**

| **5** | **6** Yield, %[a] | **7** Yield, %[a] |
|---|---|---|
| **a**, $X = H$ | 98 | 96 |
| **b** $= CH_3$ | b | 68 |
| **c** $= C(CH_3)_3$ | b | 84 |
| **d** $= CH_2OH$ | b | 43 |
| **e** $= CH_2OTBDMS$ | b | 53[c] |
| **f** $= C_6H_5$ | b | 87 |
| **g** $= OCH_3$ | b | 77 |
| **h** $= NHCOCH_3$ | b | 39 |
| **i** $= Br$ | 87 | 62 |

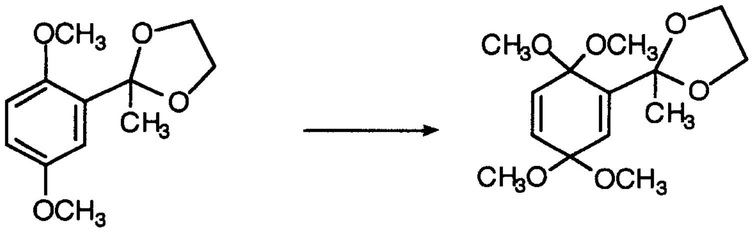
[a] Yields are based on **5** and refer to isolated, pure products. [b] The bis-ketals **6** were not purified. [c] Partial hydrolysis of the silyl ether also occurred, and **7** ($X = CH_2OH$) was also obtained in 17% yield.

products of no value. Standard protection of the carbonyl groups in these cases, however, allowed anodic oxidation to be carried out smoothly and efficiently (**8** → **9**; **10** → **11**; **12** → **13**). Unfortunately, in contrast to the situation with the bis-ketals **6**, it was not possible to devise conditions for clean and selective monohydrolysis of the ketals **9**, **11** and **13** in acceptable yields. Mixtures of 2- and 3-substituted-4,4-dimethoxycyclohexa-2,5-dienones were obtained from the bis-ketals **9a,b** and **11** derived from **8a,b** and **10** (**9a** → → 2- (43%) + 3- (57%); yield 56% from **8a**; **9b** → → 2- (37%) + 3- (63%); yield 45% from **8b**; **11** → → 2- (63%) + 3- (37%); yield 51% from **10**). Hydrolysis of the bis-ketal **13** derived from **12** gave only the 3-substituted monoketal **14**, but the yield was poor (25%).



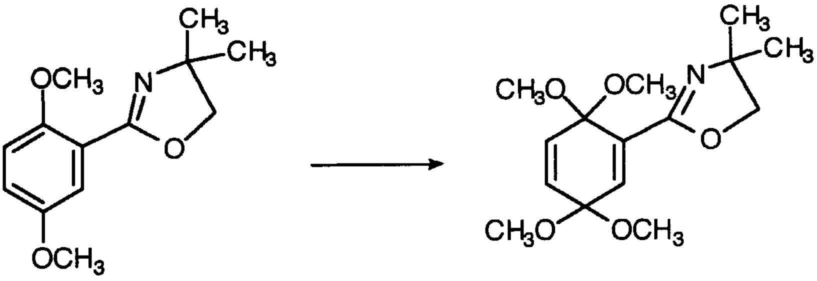
**8a**, R = H
**b**, R = CH$_3$

**9a**, R = H
**b**, R = CH$_3$



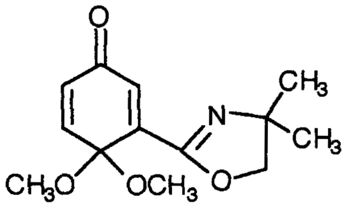
**10**

**11**



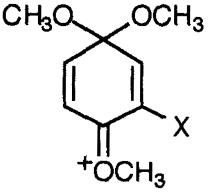
**12**

**13**

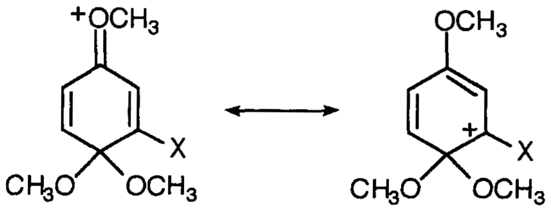


**14**

Selectivity in the hydrolysis of the bis-ketals **6** to **7** was easily established by $^1H$ nmr spectroscopy as described by Swenton *et al.*[19] and confirmed if necessary by $^1H$-$^{13}C$ nmr correlation. The transformations **6** → **7** summarised in the Table were remarkably clean, and no nmr evidence was obtained for the presence of the isomeric monoketals in the crude reaction products. The selectivity in these hydrolyses is due to a combination of steric and electronic effects. Thus, there is an unfavourable steric interaction in intermediate **15** between the X and the $=\overset{+}{O}CH_3$ group, and no electronic stabilisation of charge by the X group. By contrast, there is less of an unfavourable steric interaction in intermediate **16**, but significant electronic stabilisation of charge. In the case of **9**, **11** and **13** this favourable electronic stabilisation is absent during hydrolysis; there is, rather, a destabilising effect by the cyclic protecting group heteroatoms (β-oxygen effect).

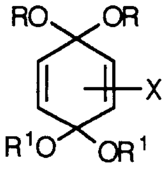


**15**



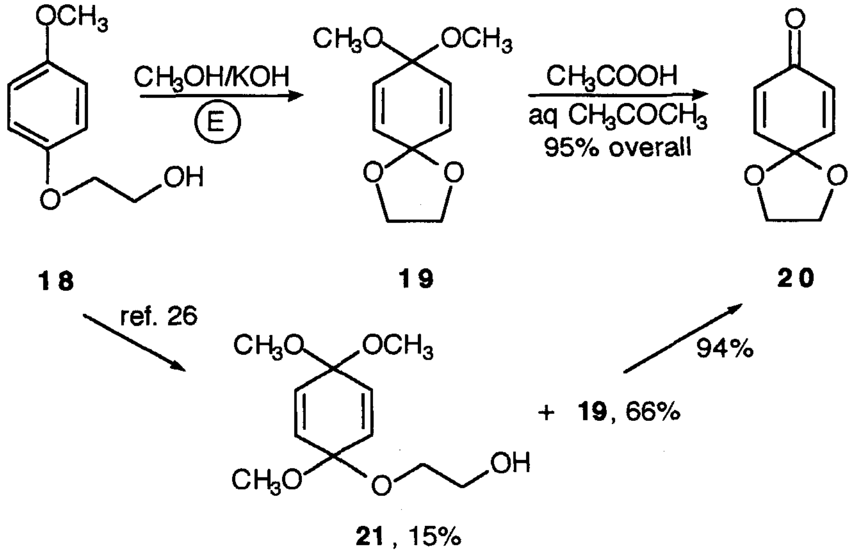
**16**

The problem of control of selective monohydrolysis of bis-ketals of the general type **17**, which can give four possible monoketals if R ≠ $R^1$, has been



**17**

solved by Swenton[1,2,26] by the simple expedient of selecting R and $R^1$ such that one of the ketals is hydrolysed much more easily than the other. The present method can be used in exactly the same way and ketals of the type **17** (R ≠ $R^1$) are readily accessible. Anodic oxidation of the dialkoxyarene **18**, for example, followed by acid catalysed hydrolysis of the intermediate bis-ketal **19** gave the pure monoketal **20** in 95% overall yield (Scheme 2). The very clean conversion of



Scheme 2

**18** to **19** in the present study contrasts with the result obtained by Swenton,[26] where electrolysis of **18** gave a mixture of **19** and the unsymmetrical bis-ketal **21**.

## Experimental

All reagents were used as commercially supplied. Reagent quality solvents were used without further purification. Chromatography was carried out using silica gel (Merck 7734). Silica gel sheets (Merck 5554) were used for tlc. Melting points are uncorrected. Mass spectra were obtained on a Kratos MS 25 spectrometer. IR spectra were recorded as nujol mulls or liquid films between NaCl plates using a Perkin Elmer 1720X FT-IR spectrometer. $^1$H NMR and $^{13}$C NMR spectra were obtained on a JEOL PMX 60 SI, a JEOL EX 90Q or a JEOL JNM EX 270 spectrometer, using $CDCl_3$ solutions with TMS as internal standard.

*Starting materials.* All starting materials with the exception of **5e**, **8a**, **8b** and **10** were either commercially available or fully characterised known compounds which were prepared by literature procedures.

**1-*tert*-Butyldimethylsilyloxymethyl-2,5-dimethoxybenzene 5e**. A solution of imidazole (1.21 g, 17.8 mmol) in dry DMF (10 ml) and then a solution of 2,5-dimethoxybenzyl alcohol (2.0 g, 11.9 mmol) in dry DMF (8 ml) were added to a solution of *tert*-butyldimethylsilyl chloride (2.69 g, 17.8 mmol) in dry DMF (20 ml) under nitrogen at room temperature. The mixture was stirred at room temperature for 18 h then diluted with dichloromethane (20 ml). The resulting mixture was washed with water (2 x 50 ml) and the organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residual oil by Kugelrohr distillation (130°C/0.05 mm Hg) gave the title compound (3.05 g, 91%) as a colourless oil (Calc for $C_{15}H_{26}O_3Si$: C, 63.79; H, 9.28. Found: C, 63.76; H, 9.24%). $\upsilon_{max}$ (neat): 2954, 2896, 2856, 2834, 1498, 1464, 1376, 1274, 1256, 1217, 1180, 1158, 1083, 1051, 838 cm$^{-1}$. δH (270 MHz): 0.15 (s, 6H, $(CH_3)_2Si$); 0.99 (s, 9H, $(CH_3)_3CSi$); 3.79 (s, 6H, $OCH_3$); 4.77 (s, 2H, $CH_2O$); 6.75 (m, 2H, $H_3$ and $H_4$); 7.14 (m, 1H, $H_6$). *m/z*: 283.3 ($M^++1$, 1.4); 282.3 ($M^+$, 6.0); 267.2 ($M^+$-$CH_3$, 2.5); 252.2 (1.8); 226.2 (14.4); 225.2 (82.5); 210.1 (100%).

**2-(2',5'-Dimethoxyphenyl)-1,3-dioxolane 8a**. A mixture of 2,5-dimethoxybenzaldehyde (5.0 g, 30.1 mmol), 1,2-ethanediol (2.0 g, 32.2 mmol) and *p*-toluenesulfonic acid monohydrate (0.01 g, 0.05 mmol) in benzene (30 ml) was heated under reflux for 4 h, during which time the water formed was collected using a Dean and Stark trap. The cooled reaction mixture was washed with 5% aqueous sodium hydroxide solution (30 ml) and water (3 x 30 ml) then dried ($MgSO_4$) and evaporated under reduced pressure. The residual oil was purified by Kugelrohr distillation (150°C/0.4 mm Hg), which gave the title compound (5.22 g, 83%) as a colourless oil (Calc for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.93; H, 6.76%). $\upsilon_{max}$ (neat): 2951, 1501, 1465, 1431, 1399, 1279, 1220, 1180, 1165, 1071, 1046 cm$^{-1}$. δH (270 MHz): 3.90 (s, 3H, $OCH_3$); 3.95 (s, 3H, $OCH_3$); 4.21 (m, 4H, $CH_2CH_2$); 6.25 (s, 1H, $H_2$); 6.97 (m, 2H, $H_{3'}$ and $H_{4'}$); 7.24 (m, 1H, $H_{6'}$). *m/z:* 211.1 ($M^++1$, 12); 210.1 ($M^+$, 100); 209.2 (44); 166.2 (46.7); 165.1 (35.9); 151.1 (24.6); 149.1 (18.5%).

**2-(2',5'-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane 8b.** A mixture of 2,5-dimethoxybenzaldehyde (3.0 g, 18 mmol), pinacol (2.59 g, 21.9 mmol) and *p*-toluenesulfonic acid monohydrate (0.01 g, 0.05 mmol) in toluene (50 ml) was heated under reflux for 5 h using a Dean and Stark water separator. Work-up and isolation of product as described for **8a** gave the title compound

(4.5 g, 94%) as a colourless solid. Recrystallisation from ether/petroleum ether (bp 40-60°C) gave colourless crystals, mp 66°C (Calc for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.87; H, 8.37%). $\upsilon_{max}$ (Nujol): 2926, 2854, 1498, 1464, 1379, 1276, 1218, 1161, 1062, 1023, 988 $cm^{-1}$. δH (270 MHz): 1.39 and 1.42 (2s, 12 H, 2 x $C(CH_3)_2$); 3.86 (s, 3H, $OCH_3$); 3.90 (3H, s, $OCH_3$); 6.36 (s, 1H, $H_2$); 6.91 (m, 2H, $H_{3'}$ and $H_{4'}$); 7.31 (m, 1H, $H_{6'}$). *m/z*: 267.2 ($M^+$+1, 16.1); 266.2 ($M^+$, 100); 235.1 ($M^+$-$OCH_3$, 13.4); 208.1 (17.4%).

**2-(2',5'-Dimethoxyphenyl)-2-methyl-1,3-dioxolane 10.** A mixture of 2,5-dimethoxyacetophenone (2.5 g, 13.9 mmol), 1,2-ethanediol (0.95 g, 15.3 mmol) and *p*-toluenesulfonic acid monohydrate (0.01 g, 0.05 mmol) in benzene (50 ml) was heated under reflux for 9 h using a Dean and Stark water separator Work-up and isolation of product as described for **8a** gave the title compound (2.42 g, 78%) as a pale yellow oil after Kugelrohr distillation (80°C/0.5 mm Hg) (Calc for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.59; H, 6.92%). δH (60 MHz); 1.78 (s, 3H, $CH_3$); 3.78 (s, 3H, $OCH_3$); 3.82 (s, 3H, $OCH_3$); 4.0 (m, 4H, $CH_2CH_2$); 6.84 (m, 2H, $H_{3'}$ and $H_{4'}$); 7.12 (m, 1H, $H_{6'}$). *m/z*: 209.2 ($M^+$-$CH_3$, 3.2); 180.2 ($M^+$- $CH_2CH_2O$, 64.9); 165.2 (100%).

**General procedure for the anodic oxidation of 1,4-dimethoxybenzenes.** The 1,4-dimethoxybenzene (**5a-i**, **8**, **10** or **12**; 1.5 to 250 mmol) was dissolved in 2% methanolic potassium hydroxide solution (200 ml) and the solution was electrolysed as described by Azadi-Ardakani and Wallace[25] until tlc analysis (silica, uv and $KMnO_4$ spray) indicated disappearance of the starting material. The solution was then concentrated under reduced pressure and the residue partitioned between water (75 ml) and dichloromethane (75 ml). The aqueous layer was separated and extracted with more dichloromethane (3 x 75 ml).

The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude bis-ketals. In a number of cases the bis-ketals were purified by either distillation or crystallisation.

**General procedure for the monohydrolysis of 1,4-benzoquinone bis-ketals**. A 2% aqueous solution of acetic acid (9 ml) was added slowly to a solution of the crude 1,4-benzoquinone bis-ketal (**6a-i**, **9**, **11** or **13**; 15 mmol) in acetone (15 ml) at 0°C. The reaction mixture was stirred for 30 min at 0°C and then at room temperature until either tlc and/or nmr analysis indicated completion of the reaction. Saturated aqueous sodium bicarbonate solution (15 ml) was then added and the resulting mixture was extracted with ether (3 x 30 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent removed by distillation under reduced pressure. The crude monoketal thus obtained was purified by column chromatography and/or distillation.

**Products**. Data are given only for new products. Spectroscopic, analytical and physical data for known products were fully in agreement with reported data.[18,19,26]

**3-*tert*-Butyl-4,4-dimethoxycyclohexa-2,5-dienone 7c**. Crude 1-*tert*-butyl-3,3,6,6-tetramethoxy-1,4-cyclohexadiene **6c** [δH (60 MHz): 1.3 (s, 9H, $C(CH_3)_3$); 3.22 and 3.32 (2s, 12H, $OCH_3$); 6.1 (m, 3H, $H_2$, $H_4$, $H_5$)] was hydrolysed as described above and the crude monoketal **7c** purified by chromatography on silica using ether/petroleum ether (bp 40-60°C) 1:1 as eluent. The pure monoketal was obtained as a colourless oil. (Calc for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.83; H, 8.44%). $\upsilon_{max}$ (Nujol): 2958, 1668, 1636, 1295, 1118, 1102, 1063 $cm^{-1}$. δH (270 MHz): 1.30 (s, 9H, $C(CH_3)_3$); 3.27 (s, 6H, $OCH_3$); 6.33 (dd, 1H, *J* 10.2 and 1.98 Hz, $H_6$); 6.39 (d, 1H, *J*

1.98 Hz, $H_2$); 6.73 (d, 1H, *J* 10.2 Hz, $H_5$). δC (67 MHz): 186.12 ($C_1$); 164.81 ($C_3$); 144.52 ($C_5$); 129.68 and 129.21 ($C_2$, $C_6$); 97.79 ($C_4$); 50.65 ($OCH_3$); 30.92 (($CH_3$)$_3$C); 29.09 (($CH_3$)$_3$*C*). *m/z*: 210.2 ($M^+$, 2.7); 195.2 (16.5); 179.2 (60.5); 154.1 (100%).

**3-Hydroxymethyl-4,4-dimethoxycyclohexa-2,5-dienone 7d.** Electrolysis of **5d** gave a mixture of products (tlc, nmr) and no attempt was made to purify bis-ketal **6d**. Monohydrolysis followed by chromatography (silica, ether/petroleum ether (bp 40-60°C), 3:1) gave the pure monoketal **7d** as a colourless oil. $\upsilon_{max}$ (neat): 2945, 1678, 1641, 1456, 1292, 1206, 1138, 1107, 1058, 1020, 964 $cm^{-1}$. δH (270 MHz): 3.27 (s, 6H, $OCH_3$); 3.46 (br. s, 1H, OH); 4.41 (d, 2H, *J* 1.98 Hz, $CH_2O$); 6.42 (dd, 1H, *J* 10.5 and 2.1 Hz, $H_6$); 6.55 (dd, 1H, *J* 2.1 and 1.98 Hz, $H_2$); 6.80 (d, 1H, *J* 10.5 Hz, $H_5$). δC (22.4 Hz): 185.15 ($C_1$); 157.87 ($C_3$): 143.12 ($C_5$); 132.05 ($C_6$); 126.32 ($C_2$); 95.28 ($C_4$); 59.44 ($CH_2OH$); 50.99 ($OCH_3$). *m/z*: 184.1 ($M^+$, 1.7); 169 ($M^+$-$CH_3$, 6.5); 155 (5.2); 154 (51.7); 153.1 ($M^+$-$OCH_3$, 100%).

**3-*tert*-Butyldimethylsilyloxymethyl-4,4-dimethoxycyclohexa-2,5-dienone 7e.** Crude 1-*tert*-butyldimethylsilyloxy-3,3,6,6-tetramethoxy-1,4-cyclohexadiene **6e** [δH (60 MHz): 0.05 (s, 6H, ($CH_3$)$_2$Si); 0.9 (s, 9H, ($CH_3$)$_3$C); 3.15 (s, 6H, $OCH_3$); 3.3 (s, 6H, $OCH_3$); 4.3 (m, 2H, $CH_2O$); 6.2 (m, 3H, $H_2$, $H_4$, $H_5$)] was hydrolysed exactly as for **7d**, and pure product was obtained as a colourless oil by chromatography (silica, ether/petroleum ether (bp 40-60°C), 1:1) (Calc for $C_{15}H_{26}O_4Si$: C, 60.37; H, 8.78. Found: C, 60.51; H, 8.87%). $\upsilon_{max}$ (neat): 2953, 2931, 1680, 1647, 1289. 1258, 1145, 1123 $cm^{-1}$. δH (270 MHz): 0.105 (s, 6H, ($CH_3$)$_2$Si); 0.94 (s, 9H, ($CH_3$)$_3$C); 3.26 (s, 6H, $OCH_3$); 4.42 (d, 2H, *J* 2.31 Hz, $CH_2O$); 6.42 (dd, 1H, *J* 10.23 and 1.98 Hz, $H_6$); 6.57 (m, 1H,

$H_2$); 6.76 (d, 1H, *J* 10.23 Hz, $H_5$). δC (67 MHz): 185.07 ($C_1$); 158.27 ($C_3$); 143.02 ($C_5$); 132.45 ($C_6$); 126.06 ($C_2$); 95.28 ($C_4$); 59.44 ($CH_2O$); 51.04 ($OCH_3$); 25.77 (($CH_3$)$_3$C); 18.22 (($CH_3$)$_3$*C*); -5.57 (($CH_3$)$_2$Si). *m/z*: 283.2 ($M^+$-$CH_3$, 1.0); 267.2 ($M^+$-$OCH_3$, 11); 242.1 (19); (241.2, 76); 211.1 (100%).

**3-Phenyl-4,4-dimethoxycyclohexa-2,5-dienone 7f.** Crude 1-phenyl-3,3,6,6-tetramethoxy-1,4-cyclohexadiene **6f** [δH (270 MHz): 3.20 and 3.38 (2s, 12H, $OCH_3$); 5.98 (d, 1H, *J* 10.5 Hz, $H_5$); 6.38 (m, 2H, *J* 10.5 and 2.5 Hz, $H_2$ and $H_4$); 7.28 and 7.68 (2m, 5H, arom)] was hydrolysed as described above and the crude monoketal **7f** purified by chromatography (silica, ether/petroleum ether (bp 40-60°C), 1:1). The pure monoketal **7f** was obtained as a colourless oil (Calc for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.77; H, 6.08%). $\upsilon_{max}$ (neat): 2997, 1667, 1632, 1602, 1446, 1383, 1293, 1273, 1213, 1077, 1009, 965, 898, 786, 696 $cm^{-1}$. δH (270 MHz): 3.24 (s, 6H, $OCH_3$); 6.49 (dd, 1H, *J* 10.2 and 2.0 Hz, $H_6$); 6.71 (d, 1H, *J* 2.0 Hz, $H_2$); 6.76 (d, 1H, *J* 10.2 Hz, $H_5$); 7.40 and 7.86 (2m, 5H, arom). δC (67 MHz); 185.37 ($C_1$); 153.19 ($C_3$); 144.60 ($C_5$); 134.45, 128.34 and 127.89 (arom); 131.36, 129.96 and 128.79 ($C_2$, $C_6$ and arom); 97.04 ($C_4$); 50.93 ($OCH_3$). *m/z*: 231.1 ($M^+$+1, 15.4); 230.1 ($M^+$, 100); 215.2 (11.4); 199.1 (51.4%).

**57:43 Mixture (by nmr) of 3-[2'-(1',3'-dioxalanyl)]-4,4-dimethoxy-cyclohexa-2,5-dienone (major) and 2-[2'-(1',3'-dioxalanyl)]-4,4-dimethoxycyclohexa-2,5-dienone (minor).** The crude mixture of monoketals obtained from hydrolysis of **9a** was purified by Kugelrohr distillation (150°C/0.3 mm Hg) (Calc for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.75; H, 6.22%). $\upsilon_{max}$ (neat): 2360, 1681, 1645, 1497, 1463, 1379, 1279, 1221, 1155, 1117, 1044, 754. δH (270 MHz): 3.31 (s, 6H major, $OCH_3$); 3.38 (s, 6H minor, $OCH_3$); 3.9 (m, 4H major and 4H minor, $H_{5'}$ and $H_{4'}$); 5.63 (s, 1H major, $H_{2'}$); 5.79 (s, 1H minor, $H_{2'}$); 6.28 (d, 1H minor, *J* 10.23 Hz, $H_6$); 6.42 (dd, 1H major, *J* 10.2 and 2.0 Hz, $H_6$); 6.63 (d, 1H major *J* 2.0 Hz, $H_2$); 6.79 (d, 1H major, *J* 10.23 Hz, $H_5$); 6.83 (m, 1H minor, $H_5$); 7.02 (d, 1H minor, *J* 3.0 Hz, $H_3$). *m/z*: 211.1 ($M^+$-$CH_3$, 2.1); 210.1 (9.1); 209.1 (4.3); 196.1 (8.5); 195.1 ($M^+$-$OCH_3$, 65.6); 194.1 (40.7%).

**1-[2'-(4',4',5',5'-Tetramethyl-1',3'-dioxalanyl)]-3,3,6,6-tetramethoxy-1,4-cyclohexadiene 9b**. The crude product from electrolysis of **8b** was purified by Kugelrohr distillation (130°C/0.4 mm Hg) (Calc for $C_{17}H_{28}O_6$: C, 62.18; H, 8.59. Found: C, 62.48; H, 8.64%). $\upsilon_{max}$ (neat): 2981, 2940, 2831, 1465, 1389, 1378, 1337, 1219, 1154, 1107, 1081, 1043, 965 $cm^{-1}$. δH (270 MHz): 1.24 and 1.25 (2s, 12H, 4x$CH_3$, $C_{4'}$ and $C_{5'}$); 3.22 and 3.32 (2s, 12H, $OCH_3$); 5.64 (d, 1H, *J* 0.66 Hz, $H_{2'}$); 5.96 (d, 1H, *J* 10.56 Hz, $H_5$); 6.24 (dd, 1H, *J* 10.56 and 2.97 Hz, $H_4$); 6.62 (dd, 1H *J* 2.97 and 0.66 Hz, $H_2$). δC (67 MHz): 139.39 ($C_1$); 132.0, 130.71 and 129.88 ($C_2$, $C_4$, $C_5$); 95.96 and 93.26 ($C_3$ and $C_6$); 94.61 ($C_{2'}$); 81.94 ($C_{4'}$, $C_{5'}$); 51.04 and 49.90 ($OCH_3$); 24.08 and 21.98 (C-$CH_3$). *m/z*: 297.3 ($M^+$-$OCH_3$, 6); 296.3 (24); 295.3 (7.9); 266.2 ($M^+$-2x$OCH_3$, 32); 265.3 (86.2%).

**37:63 Mixture (by nmr) of 2-[2'-(4',4',5',5'-tetramethyl-1',3'-dioxalanyl)]-4,4-dimethoxycyclohexa-2,5-dienone (minor) and 3-[2'-(4',4',5',5'-tetramethyl-1',3'-dioxalanyl)]-4,4-dimethoxycyclohexa-2,5-dienone (major)**. The crude mixture of monoketals obtained from hydrolysis of **9b** was purified by Kugelrohr distillation (150°C/0.5 mm Hg). δH (270 MHz): 1.26 (4s, 12H major and 12H minor, C-$CH_3$); 3.22 and 3.32 (2s, 6H major, $OCH_3$); 3.30 and 3.36 (2s, 6H minor, $OCH_3$); 5.64 (s, 1H major, $H_{2'}$); 5.87 (s, 1H minor, $H_{2'}$); 5.96 (d, 1H minor, *J* 10.56 Hz, $H_6$); 6.23 (dd, 1H major, *J* 10.56 and 2.7 Hz., $H_6$); 6.62 (d, 1H major, *J* 2.7 Hz, $H_2$); 6.77 (m, 1H minor and 1H major, 2 $H_5$); 7.05 (d, 1H minor, *J* 2.3 Hz, $H_3$). *m/z:* 282.2 ($M^+$, 1.1); 266.2 (23.9); 265.2 (74.3); 252.2 (14.4); 251.2 ($M^+$-$OCH_3$, 27.8); 250.2 (11.9).

**1-[2'-(2'-Methyl-1',3'-dioxalanyl)]-3,3,6,6-tetramethoxy-1,4-cyclohexadiene 11.** The crude bis-ketal was purified by Kugelrohr distillation (130°C/0.2 mm Hg). $\upsilon_{max}$ (neat): 2940, 2831, 1465, 1394, 1192, 1111, 1044, 966 $cm^{-1}$. δH (270 MHz): 1.66 (s, 3H, $C_{2'}$-$CH_3$); 3.23 and 3.32 (2s, 12H, $OCH_3$); 3.92 (m, 4H, $H_{4'}$ and $H_{5'}$); 5.98 (dd, 1H, *J* 10.56 and 0.8 Hz, $H_5$); 6.22 (dd, 1H, *J* 10.56 and 2.64 Hz, $H_4$); 6.50 (dd, 1H, *J* 2.64 and 0.8 Hz, $H_2$). δC (67 MHz): 139.82 ($C_1$); 130.75, 130.28 and 129.58 ($C_2$, $C_4$, $C_5$); 96.62 and 93.10 ($C_3$, $C_6$ and $C_{2'}$); 64.44 ($C_{4'}$, $C_{5'}$); 50.78 and 49.63 ($OCH_3$); 25.72 (C-*C*$H_3$). *m/z*: 271.2 ($M^+$-CH3, 3); 255.2 ($M^+$-$OCH_3$, 2); 209.1 (22); 197.1 (4%).

**Monohydrolysis of 11.** The crude mixture (63:37 by nmr) of monoketals from hydrolysis of **11** was purified by Kugelrohr distillation (150°C/0.2 mm Hg) [(Calc for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.08; H, 6.78%); *m/z*: 225.2 ($M^+$-$CH_3$, 9.6); 209.2 ($M^+$-$OCH_3$, 14.6)] and separated into the pure monoketals by chromatography (silica, ether/petroleum ether (bp 40-60°C)/triethylamine, 49:49:2). This gave, as colourless oils, *2-[2'-(2'-methyl-1',3'-dioxalanyl)]-4,4-dimethoxycyclohexa-2,5-dienone* as the major component [δH (270 MHz): 1.68 (s, 3H, $C_{2'}$-$CH_3$); 3.38 (s, 6H, $OCH_3$); 3.9 (m, 4H, $H_{4'}$ and $H_{5'}$); 6.25 (d, 1H, *J* 10.4 Hz, $H_6$); 6.78 (dd, 1H, *J* 10.4 and 3.3 Hz, $H_5$);

7.0 (d, 1H, *J* 3.3 Hz, $H_3$)] and *3-[2'-(2'-methyl-1',3'-dioxalanyl)]-4,4-dimethoxycyclohexa-2,5-dienone* as the minor component [δH (270 MHz): 1.69 (s, 3H, $C_{2'}$-$CH_3$); 3.31 (s, 6H, $OCH_3$); 3.9 (m, 4H, $H_{4'}$ and $H_{5'}$); 6.37 (dd, 1H, *J* 10.23 and 2.31 Hz, $H_6$); 6.60 (d, 1H, *J* 2.31 Hz, $H_2$); 6.79 (d, 1H *J* 10.23 Hz, $H_5$)].

**1-[2'-(4',4'-Dimethyl-2'-oxazolinyl)]-3,3,6,6-tetramethoxy-1,4-cyclohexadiene 13**. The crude bis-ketal **13** was purified by Kugelrohr distillation (150°C/0.5 mm Hg) (Calc for $C_{15}H_{23}NO_5$: C, 60.59; H, 7.80; N, 4.71. Found: C, 60.73; H, 7.77; N, 4.74%). $\upsilon_{max}$ (neat): 2966, 2831, 1627, 1464, 1394, 1293, 1202, 1108, 1085, 1039, 967 $cm^{-1}$. δH (270 MHz): 1.29 (s, 6H, $C_{4'}$-$(CH_3)_2$); 3.20 and 3.31 (2s, 12H, $OCH_3$); 3.95 (s, 2H, $H_{5'}$); 5.92 (d, 1H, *J* 10.7 Hz, $H_5$); 6.22 (dd, 1H, *J* 10.7 and 2.8 Hz, $H_4$); 6.93 (d, 1H, *J* 2.8 Hz, $H_2$). δC (67 MHz): 159.17 ($C_1$); 137.27, 131.11 and 130.87 ($C_2$, $C_4$ and $C_5$); 130.49 ($C_{2'}$); 95.58 and 92.51 ($C_3$ and $C_6$); 78.56 ($C_{5'}$); 67.39 ($C_{4'}$); 51.14 and 49.87 ($OCH_3$); 27.96 and 27.89 (C-*C*H3). *m/z:* 282.2 ($M^+$-$CH_3$, 36.8); 267.1 (11.5); 266.2 ($M^+$-$OCH_3$, 69.1); 251.2 (9.4); 237.1 (15.3); 236.1 ($M^+$-$OCH_3$-2x$CH_3$, 100%).

**3-[2'-(4',4'-Dimethyl-2'-oxazolinyl)]-4,4-dimethoxycyclohexa-2,5-dienone 14**. Monohydrolysis of **13** as described above followed by chromatography (silica, ether/petroleum ether (bp 40-60°C)/dichloromethane, 1:1:1) gave the pure monoketal **14** as a colourless oil. $\upsilon_{max}$ (neat): 2969, 2934, 2833, 1671, 1649, 1599, 1463, 1295, 1208, 1087, 1009, 981, 916, 821, 727 $cm^{-1}$. δH (270 MHz): 1.37 (s, 6H, $C_{4'}$-$(CH_3)_2$); 3.31 (s, 6H, $OCH_3$); 4.05 (s, 2H, $H_{5'}$); 6.46 (dd, 1H, *J* 10.3 and 2.1 Hz, $H_6$); 6.78 (d, 1H, *J* 10.3 Hz, $H_5$); 6.96 (d, 1H, *J* 2.1 Hz, $H_2$). δC (67 MHz): 184.87 ($C_1$); 158.40 ($C_3$); 145.36

($C_5$); 142.34 ($C_{2'}$); 134.29 and 131.05 ($C_2$, $C_6$); 95.15 ($C_4$); 78.83 ($C_{5'}$); 68.21 ($C_{4'}$); 51.48 ($OCH_3$); 28.0 (C-$CH_3$). *m/z*: 238.2 (1.2); 237.2 (2.2); 236.2 ($M^+$-$CH_3$, 12.1); 222.2 (17.2); 221 ($M^+$-2x$CH_3$, 100%).

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