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Studies in the Oxidative Ring-Opening of Catechols and *o*-Benzoquinones. Lead Tetraacetate versus the Copper(I) Chloride/Pyridine/Methanol System.

James G. Walsh,[a] Patrick J. Furlong,[a] Louise A. Byrne[b] and Declan G. Gilheany*[a]

[a]*Department of Chemistry, National University of Ireland, Maynooth, Co. Kildare, Ireland*
[b]*Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland*

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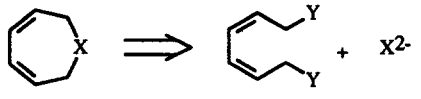
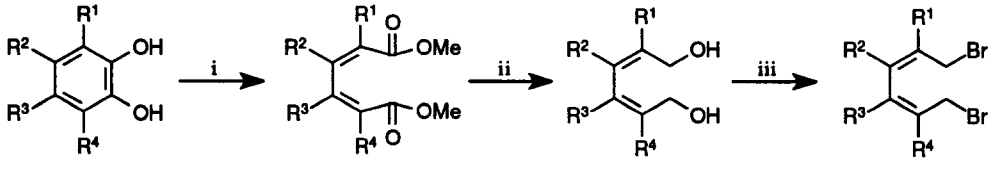
Abstract. Lead tetraacetate oxidative ring-opening of a series of substituted catechols provides the corresponding substituted *cis,cis*-2,4-diene-1,6-dioates (**1-10**) in fair to good yields. A number of improvements on Wiessler's procedure for this reaction are reported. The analogous copper(I) chloride/pyridine/methanol ring-opening was found to be ineffective as a general synthetic method for this transformation. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

We have previously communicated[2] a general strategy for the construction of seven-membered rings according to the following [6+1] disconnection:



The utility of the strategy depends on the ready availability of a precursor 1,6-biselectrophile which has the correct *cis,cis* stereochemistry[3] of the double bonds. We chose a series of *cis,cis*-2,4-diene-1,6-dibromides as electrophiles and showed that, in combination with various nucleophiles, they can serve as precursors of various heterocycles and carbocycles.[2] In order to avoid complications of isomer numbers and cumbersome routes, we chose to make the dibromides from substituted catechols by the short synthetic sequence shown in Scheme 1. It can be seen that the crucial *cis,cis* stereochemistry is derived from the first step of this sequence and we report now in detail our studies on a comparison of methods for the oxidative ring-opening of catechols and their derived quinones. Details of the latter part of the sequence in Scheme 1 will be the subject of a forthcoming publication.[4]



Scheme 1. i: $Pb(OAc)_4$, MeOH, C_7H_8, 25 °C; ii, DIBAL-H, C_7H_8, 25 °C; iii, PBr_3, Et_2O, 0 °C.

There are many methods available for this ring-opening reaction including both enzymatic[5] and non-enzymatic procedures.[6] We eventually settled on Wiessler's method[7,8] using lead tetraacetate. We also expended a considerable amount of effort on the biomimetic copper system originally reported by Tsuji and Takayanagi[9] because this seemed to have the potential to be completely specific for the catechol functional group. However we found that problems of limited substrate scope and cumbersome and delicate processes

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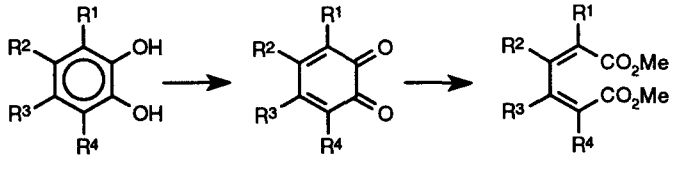
(*vide infra*) rendered it ineffective. In any future work we would explore the possibility of a dioxirane-based method which would avoid the toxicological and environmental problems of lead and which has been used for catechol ring-opening.[10]

OXIDATION OF CATECHOLS/QUINONES WITH LEAD TETRAACETATE

Lead tetraacetate (LTA) is a versatile oxidant in organic chemistry.[11] However, although its use in the cleavage of catechols/quinones was successfully developed in the late 1970s by Wiessler,[7,8] this has not been recognised.[11,12] We presume that this is because the only published material is a very short paper[7] relating to the quinones only. In fact, Wiessler oxidised substituted *o*-benzoquinones using LTA to give the related *cis,cis*-hexa-2,4-diene-1,6-diesters in good to very good yields.[7] The procedure also proved successful in the cleavage of the catechols, with use of twice the number of equivalents of lead tetraacetate[8] in the sequential oxidation process shown in Scheme 2. A range of multiple alkyl substituents (Me, ^{t}Bu, Ph and combinations) was examined and yields from the catechols were comparable to or slightly reduced from those from the quinones.[7,8] Subsequently Popkova *et al.*[13] and Jaroszewski and Ettlinger[14] reported single examples of this use for LTA. We report now further examples which extend the scope of this reaction to include the unsubstituted and singly substituted cases and those with electron donating/withdrawing substituents. We also record some improvements to the experimental procedures which increase the yields and facilitate work-up. A full listing of all substrates previously studied is also included.



1-12

Scheme 2

Experimental procedures.

Wiessler's method calls for the addition of the organic substrate (catechol or quinone) dissolved in methanol and benzene to a chilled, stirred solution of lead tetraacetate in methanol and benzene. Jaroszewski and Ettlinger[14] subsequently reported (for one substrate) that slow addition gave a poor yield for the catechol case while a reasonable yield was obtained from the quinone in the reverse addition mode. Our initial preparations (procedure A) followed Wiessler's protocol fairly closely. We then went on to develop a somewhat improved procedure (B) which was found to give better yields generally and allowed greater ease of isolation.

The most important aspect of procedure B is that the lead tetraacetate is recrystallised just prior to its use, very carefully freed of acetic acid and dried *in vacuo*. Although there may be a number of contaminants removed by this purification, we are certain that the removal of lead(II) oxide and acetic acid are major factors since both lead to side-reactions.[11] Similarly the presence of water is detrimental to the oxidising power of the lead complex as this leads to the production of these undesirable impurities. Consequently all solvents and substrates need to be dry and a slight excess of oxidising agent is necessary to counteract any adventitious water. Attention to these details allowed the reactions to be carried out at room temperature and in the more benign toluene as reaction solvent. Also, in the work-up, changing the extraction solvent from chloroform to ether and the addition of a few millilitres of ethylene glycol before washing with water resulted in an easier work-up and useful increases in yield in some cases.

In many cases the second stage of the oxidation process (i.e. the ring cleavage of the quinone) is more difficult and more time consuming. However the progress of the reaction can be easily followed by the persistence of a red colour, indicative of the presence of quinone. In procedure A it was often found necessary to add further reagent (10-15%) to complete reaction. However in procedure B, the use of a slight initial excess (10%) of LTA sufficed.

A range of catechols and quinones were subjected to oxidation using this lead tetraacetate, methanol, benzene/toluene system and the results are shown in Table 1. Typically with alkyl-substituted substrates reaction took from 1-2 days but was over in less than 30 minutes with electron deficient cases. The yields of derived diesters **1-12** were excellent with seven cases over 90% after purification. With three exceptions (*vide infra*), no other isomers or side-products were detected, other than some unreacted quinone which elutes more slowly than the diester products on chromatography. This was true even in the lower-yielding cases. In some cases (**3** and **7**) both catechol and related quinone were oxidised with similar yields but it cannot be assumed that this will be true in all cases since both methyl-substituted quinones gave poor yields. Mainly the catechols were chosen for this study because they are more readily available and tend to be more stable than the quinones, particularly the less substituted examples which may be prone to polymerisation. Jaroszewski and Ettlinger[14] reported a yield of only 8% when they used the 4-methyl substrate although a yield of 57% was obtained when the corresponding quinone was used. In our hands the quinone gave only a trace of product in a complex mixture but the same catechol afforded a superior yield of 76% using our modified process.

Table 1. Yields[a] of Diesters **1-12** Obtained from the Oxidative Ring-Cleavage of Substituted Catechols and Quinones with Lead Tetraacetate According to Scheme 2.

Product	R^1	R^2	R^3	R^4	Yield A %	Yield B %	Lit Yield %
1	H	H	H	H	60[b]	73[b]	
2	H	^{t}Bu	H	H	90	93	
3[c]	^{t}Bu	H	^{t}Bu	H	90	95	90[d]
3	^{t}Bu	H	^{t}Bu	H	70-95	95	90[e]
4	H	Me	H	H	39	76[h]	8
4[c]	H	Me	H	H		<5	57[f,g]
5	Me	H	H	H	50[b]	54[h]	
5[c]	Me	H	H	H		<5	
6	MeO	H	H	H	92[b]		
7	Cl	Cl	Cl	Cl		96	
7[c]	Cl	Cl	Cl	Cl	98		
8	Br	Br	Br	Br	92	95	
9	Mor[i]	H	H	Mor[i]	62[b]		
10[c]	benzo		H	H		96	
11	H	NO_2	H	H	91[j]		
12[c]	H	MeO	MeO	H	54[k]		

[a] unless noted otherwise yields are after isolation by chromatography; for procedures A/B: see experimental section; [b] yield after chromatography and recrystallisation; [c] quinone used with 1 eqv. of oxidant; [d] ref. 7; [e] ref. 8; [f] ref. 14; [g] reverse addition; [h] yield estimated by ^{1}H-nmr before chromatography [i] Mor: morpholinomethyl; [j] combined yield of isomers; [k] combined yield of products.

Product characterisation.

All of the single product diesters **1-10** were fully characterised and their spectroscopic and elemental analysis data were consistent with the proposed structures. The mass spectra provided the expected fragmentation patterns for all the structures with the expected distinctive halogen isotope profiles for the tetrabromo- and tetrachloro-analogues. Likewise the IR spectra were consistent with the products with the presence of the definitive carbonyl signals. ^{13}C-NMR spectra in each case showed the presence of four alkene carbons between 110 and 165 ppm with the expected carbonyl signals at 160 to 180 ppm. The

methoxy carbons of the ester group appeared between 50 and 55 ppm. The other carbon atoms present due to the various substituents occurred in the expected positions.

The ^{1}H-NMR spectra, instrumental in the correct determination of the correct stereoconfiguration of the products, showed clearly the presence of the two methoxy ester groups with usually a pair of singlets, unless symmetrically substituted, occurring between 3.5 and 4.0 ppm. The chemical shift values and coupling constants for the alkene protons, where they exist, are shown in Table 2 and occur in the range 5.5 to 8.0 ppm. Of the four alkene hydrogens H2 and H3 are found furthest downfield notably as far as 7.9 ppm in the unsubstituted diester **1**. The two other hydrogens, H1 and H4, are found further upfield and, as can be seen from Table 2, most are at 6.0 ppm or less.

Table 2. ^{1}H-NMR Data[a] for the Alkene Hydrogens in Dimethyl *cis,cis*-hexa-2,4-diene-1,6-dioates[b].

Diester	R^1 = H	R^2 = H	R^3 = H	R^4 = H	$^3J_{H3\text{-}H4}$
1	6.00	7.91	7.91	6.00	10.3
2	5.84		6.75	5.98	12.3
3		6.25		5.75	
4	5.80		7.14	5.87	12.0
2*Z*,4*Z*-**4**[c]	5.83		7.17	5.92	12.2
2*Z*,4*E*-**4**[c]	5.95		8.64	6.18	16.0
2*E*,4*E*-**4**[c]	6.05		7.29	6.22	15.8
5		7.37-7.69	7.37-7.69	5.82	10.1
6		7.22-7.68	7.22-7.68	5.63	10.1
9		7.33	7.33		
10			7.57	6.04	12.1
E-**10**[d]			8.45	6.27	16.0
11	6.35		7.67	6.71	6.99

[a] 80 or 270 MHz, $CDCl_3$; δ ppm, J: Hz; [b] structures given in Table 1/Scheme 2; [c] data from ref. 14; [d] data from ref. 40

The products are assigned the *cis,cis* stereochemistry based on literature comparison of chemical shift and coupling constant data, in particular the data of Jaroszewski and Ettlinger.[14] These workers oxidised 4-methyl-*o*-benzoquinone producing the (2*Z*,4*Z*)-hexa-2,4-diene-1,6-diester and, by subsequent irradiation, the corresponding (2*Z*,4*E*) and (2*E*,4*E*)-isomers. Their ^{1}H-NMR data (270 MHz) for the alkene hydrogens is also reproduced in Table 2. Unfortunately the 2*E*,4*Z* structure was not available for comparison. Allowing for the difference in spectrometer power, there is excellent agreement between the two sets of data for the (2*Z*,4*Z*)-isomer. Similar agreement was obtained for the methyl and carbomethoxy hydrogen shifts. The chemical shift values for the alkene hydrogens of the various other substituted hexa-2,4-diene-1,6-diesters shown in Table 2 are consistent with the values for compound (2*Z*,4*Z*)-**4** and agree with literature comparisons where available (see experimental).

More significant in Table 2 is that the coupling constants ($^3J_{H3\text{-}H4}$), where available, are indicative of the desired *cis,cis* configuration i.e. ^3J = 6-12 Hz not ^3J = 12-18 Hz which would imply a *trans* configuration. Unfortunately due to their substitution pattern, no data are available for the tetrahalo substituted compounds. It was also possible in some cases to determine the long range coupling constants (^4J) for the di-*tert*-butyl (**3**), *tert*-butyl (**2**) and unsubstituted (**1**) compounds. These were 1.7, 1.85 and 2.3 Hz respectively which are consistent with the value of $^4J_{H1\text{-}H3}$ = 2.1 Hz observed by Jaroszewski and Ettlinger[14] for (2*Z*,4*Z*)-**4**, whereas the (2*Z*,4*E*)- and (2*E*,4*E*)-isomers gave values of $^4J_{H1\text{-}H3}$ = 0.9 and 0.7 respectively which are outside the error range of our data.

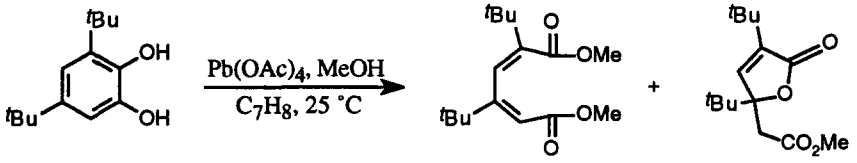
Further evidence for the *cis,cis* configuration is provided by the data of Landesberg and Kellner[15] who generated and characterised dimethyl (2*E*,4*E*)-hexa-2,4-diene-1,6-dioate by the action of sodium methoxide

on the related hexynedioic ester. This has alkene hydrogens appearing as two doublets at 7.32 ppm and 6.18 ppm with coupling constant ^3J = 15.5 Hz again incompatible with the data for compound **1** generated in this study from unsubstituted catechol. Therefore from the evidence of previous work it can be concluded that the products of lead tetraacetate-assisted oxidative ring cleavage of the catechols and quinones reported here bear the desired *cis,cis* configuration.

Side product from 3,5-di-tert-butylcatechol.

On a number of occasions, while carrying out the oxidation of 3,5-di-*tert*-butyl-catechol, along with the expected (Z,Z)-diene-1,6-dioate, a second product was formed in varying yields, identified as the lactone **13**, Scheme 3. As we shall see, this lactone is the major product in the copper-based oxidation of the same substrate so that its appearance during this lead work is relevant to any mechanistic speculations in the copper system (*vide infra*). The formation of lactone is prevented by the use of freshly recrystallised LTA.

The diester and lactone proved very difficult to separate by column chromatography as they have almost identical R_f values with all the solvent systems used. However, it was successfully separated by simply placing the crude oil, dissolved in hexane/ether (1:1), in a freezer which caused the lactone to crystallise as a white solid leaving behind the (liquid) diester in solution.



Scheme 3 **3** **13**

Other side products.

Two substrates gave more than one product namely 4-nitrocatechol and 4,5-dimethoxyquinone. In the former case ^{1}H-NMR analysis showed that the crude material contained two diester compounds. Despite the use of many different chromatography methods, these proved impossible to separate. It is probable that they are isomers because although they were not separated it was possible to assign signals on the ^{1}H-NMR from visual analysis through the varying proportions of each which resulted from different runs of the reaction. The expected product, dimethyl (2*E*,4*Z*)-3-nitrohexa-2,4-diene-1,6-dioate (**11**), could be discerned along with another compound with similar characteristics. Thus in it there are two singlets at 3.48 ppm and 3.92 ppm and a pair of doublets at 6.52 ppm and 7.80 ppm with a coupling constant ^3J = 7.1 Hz. However there would appear to be a proton missing as any expected product e.g. an isomer of the normal product would have three alkene hydrogen signals. The integrals also presented a difficulty with the signal at 3.48 ppm having a larger than expected value. Definitive identification of this side-product must therefore await isolation of a pure sample of this material.

On oxidation 4,5-dimethoxy-*o*-benzoquinone gave a crude reaction mixture containing at least four main products. It is likely that this is because there are alternative sites of ring cleavage due to the presence of the methoxy groups or that acetoxylation occurred.[11] Finally when 2,3-dihydroxynaphthalene was used as starting material only a small amount of crude product was obtained and from the ^{1}H-NMR spectrum it was concluded that no ring cleavage occurred. This is unsurprising because the ring opened product results in a greater loss of aromatic stabilisation energy in this case.

Conclusion.

The lead tetraacetate oxidative ring-opening of catechols/quinones is a robust and reliable procedure for the synthesis of substituted *cis,cis*-2,4-diene-1,6-dioates. The results reported above double (to >20 cases) the number of substrate substitution patterns which have been reported to date for this conversion and extend the reaction to non-alkyl substituted cases. We have also detailed some modifications to the experimental procedures which increase the yields by 10-15% and make work-up easier. Table 3 records the substrates which have been now successfully subject to this reaction. A surprising aspect of the results reported here is

the use of methyl-substituted substrates and, especially, toluene as solvent because it is well known[11] that LTA in acetic acid can oxidise the benzylic position. We believe that the key to success in the reactions reported here is the absence of acetic acid in the system and the use of mild conditions.

Table 3. Substrates[a] and Best Yields of Diesters Obtained to date from the Oxidative Ring-Cleavage of Substituted Catechols and Quinones with Lead Tetraacetate.

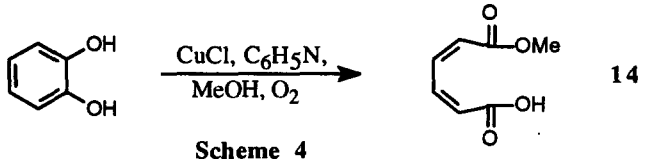
R^1	R^2	R^3	R^4	Yield from catechol %	Yield from quinone %
H	H	H	H	73[b]	
Me	H	H	H	53[b]	
H	Me	H	H	76[b]	57[d]
Me	H	Me	H		75[e]
Me	H	H	Me	65[f]	60[e]
H	Me	Me	H		70[e]
H	^{t}Bu	H	H	93[b]	
^{t}Bu	H	^{t}Bu	H	95[b,f]	90[b,e]
^{t}Bu	H	H	^{t}Bu	40[f]	60[e]
^{t}Bu	H	Me	H	60[f]	
^{t}Bu	H	H	Me	65[f]	
Me	H	^{t}Bu	H	60[f]	
H	Ph	H	H	80[f]	
H	-$(CH_2)_3$-		H	60[f]	60[e]
H	-$(CH_2)_4$-		H	65[f]	
H	-$(CH_2)_5$-		H	68[f]	70[d]
H	-$(CH_2)_6$-		H	50[f]	
benzo		H	H		96[b]
Mor[g]	H	H	Mor[g]	62[b,c]	
MeO	H	H	H	92[b,c]	
F	F	F	F	37-70[h]	37-70[h]
Cl	Cl	Cl	Cl	96[b]	98[b]
Br	Br	Br	Br	95[b]	
H	NO_2	H	H	91[b,c,i]	

[a] For structures, see Scheme 2; [b] this work; [c] by unoptimised procedure A; [d] ref. 14; [e] ref. 7; [f] ref. 8; [g] Mor: morpholinomethyl; [h] ref. 13; [i] combined yield of isomers.

OXIDATION OF CATECHOLS/QUINONES WITH COPPER(I) CHLORIDE/PYRIDINE/METHANOL

In 1974 Tsuji and Takayanagi[9] reported the oxidation of catechol using this system. The product formed, *cis,cis*-monomethyl muconic acid (**14**, Scheme 4) had the same degree of specificity as those generated in nature by enzymes and consequently this method was claimed by Tsuji and Takayanagi to be the first model for the action of the enzyme pyrocatechase.[9,16,17] Further work, particularly on the reaction mechanism of the system, by Rogic and Demmin showed that the reaction could proceed without molecular oxygen and hence they discounted Tsuji's claim that this was a suitable model for pyrocatechase.[18-22] Other studies on the system were also carried out by Speier and Tyeklar[23-25] and others.[26] Notwithstanding the relevance or not of this system to biological activity, it had an attractive potential for us as a specific oxidative ring

cleavage system useful for the formation of *cis,cis*-dienes from catechol fragments in large multifunctional substrates in a mode reminiscent of biological systems.



14

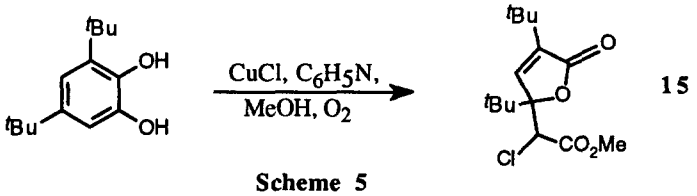
Scheme 4

Usefulness as a synthetic method.

For the purpose of this work the method of Tsuji and Takayanagi[9,16,17] does provide a suitable means for obtaining stereospecifically in good yield (>70%) a substrate which can be adapted to form the reactive six-carbon synthon required. However, both the method of reaction and work-up were found to be cumbersome. Thus in the case of the unsubstituted catechol, fine control of addition of the substrate to the oxidising agent is required. Catechol is initially easily oxidised to the *o*-quinone which can then be attacked by another molecule of catechol and undergo oxidative polymerisation. To prevent this a high dilution technique has to be employed, hence the necessity for slow addition and the presence of large amounts of the unsociable solvent pyridine, the removal of which was slow and cumbersome and exposed a potentially sensitive system to elevated temperatures. Efforts by Tsuji and Takayanagi to replace pyridine as a solvent by substituted pyridines or by benzene, acetonitrile or tetrahydrofuran led to a significantly diminished yield.[17] The product monomethyl muconic ester **14** also had to be isolated from the evaporation residue by extraction with hot hexane adding further to an already lengthy procedure. It was found possible to improve on the reported yield to about 75% but often it fell well below 60% if the control of addition was not precise enough.

Side product from 3,5-di-tert-butylcatechol.

Most disappointing however was the observation that other substituted catechols were not suitable substrates for the system. Tsuji and co-workers had tried a small number of substituted catechols with varying degrees of success. It was found that the yield dropped using halogen substituents and no product was formed when nitrocatechol was reacted.[17] The use of unsymmetrically substituted systems such as 4-methylcatechol while giving high overall yields (79%) produced a mixture of isomers.[17] This, in itself, is not a great disadvantage since the next step in many cases is reduction to the diol or conversion to diester by treatment with diazomethane. However the 3,5-di-*tert*-butyl substrate gave none of the expected monomethyl muconic ester. Instead a small amount (15%) of white solid was formed which when characterised was found to be chlorolactone **15**, Scheme 5:



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Scheme 5

This product had been previously observed by Rogic and Demmin during one of their studies to ascertain the identity of the oxidising agent in this system.[22] They had shown in individual steps that catechols could be converted to quinones and that the latter could be oxidised to muconic anhydrides which, when subjected to a copper complex-assisted oxidation, yielded initially muconic acid esters which readily lactonised.[24] They also found that chlorolactone **15** was formed when they treated 3,5-di-*tert*-butylmuconic anhydride with a pre-made complex, pyridine cupric methoxy chloride $(PyCuClOMe)_2$. Lactones were known to form from substituted anhydrides when oxidised and it was assumed that the presence of excess copper complex caused the halogenation of this lactone.[22]

The isolation of chlorolactone **15** directly from the catechol reported here complements the work of Rogic and Demmin in that we have shown that direct treatment of 3,5-di-*tert*-butylcatechol with oxygen in a pyridine and methanol solution of copper(I) chloride results in a low yield of the same product. During the reaction a significant amount (up to 30%) of small blue crystals were isolated and characterised as bis(pyridine) cupric chloride, a side-product also detected by Rogic and Demmin in some of their work.[19] The overall yield of organic products in this reaction was low (20%) but attempts to increase it or locate the remainder of the organic product failed. Evaporation of the bright blue aqueous layer gave initially a dark green solution and ultimately a bright orange solid characterised as the inorganic complex, bis(pyridinium) tetrachlorocuprate.

Use of pre-made copper complexes.

In an attempt to circumvent the work-up procedure and reduce the relatively large amounts of solvent required, some pre-made copper complexes were tried for this oxidation using the 3,5-di-*tert*-butyl substrate since it was deemed the most difficult to oxidise with control. The results are shown in Table 4 along with our *in-situ* results (entries 1/2) and some others for comparison.

The copper complex, pyridine copper methoxy chloride[27] $(PyCuClOMe)_2$, was used by Rogic and Demmin[18] to oxidise both unsubstituted and monosubstituted catechols to the corresponding muconic esters or lactones. However in our hands, this method applied to both 3,5-di-*tert*-butylcatechol and the corresponding quinone using various solvent combinations gave no ring-cleavage and the product obtained in all reactions was 3,5-di-*tert*-butyl-*o*-benzoquinone (entries 6-10). In extensive studies Rogic and Demmin[19] have shown how ring-cleavage can be shut down by the intervention, within the complex catalytic cycles, of inert copper catecholate species.

Table 4. Product yields in the oxidation of 3,5-di-*tert*-butylcatechol/quinone with various systems.

Entry	Oxidation system[a]	Substrate	Product	Yield %
1	$CuCl/pyr/MeOH/O_2$	catechol	chlorolactone (**15**)	15
2	$Pb(OAc)_4/C_7H_8/MeOH$	catechol	lactone (**13**)	0-25
3[b]	$CuCl/pyr/MeOH/O_2$	catechol	lactone (**13**)	55
4[b]	$CuCl/pyr/MeOH/O_2$	quinone	lactone (**13**)	35
5[c]	$(PyCuClOMe)_2/pyr/N_2$	anhydride[d]	chlorolactone (**15**)	95
			lactone (**13**)	5
6	$(PyCuClOMe)_2/CH_2Cl_2/MeOH$	catechol	quinone	64
7	$(PyCuClOMe)_2/pyr/MeOH$	catechol	quinone	86
8	$(PyCuClOMe)_2/pyr/MeOH/Py_2CuCl_2$	catechol	quinone	82
9	$(PyCuClOMe)_2/pyr/MeOH$	quinone	quinone	97
10	$(PyCuClOMe)_2/pyr/MeOH/Py_2CuCl_2$	quinone	quinone	92
11[b]	$CuClOMe/pyr/N_2$	quinone	muconate (**3**)	80
12	$CuClOMe/pyr/N_2$	quinone	lactone (**13**)	57

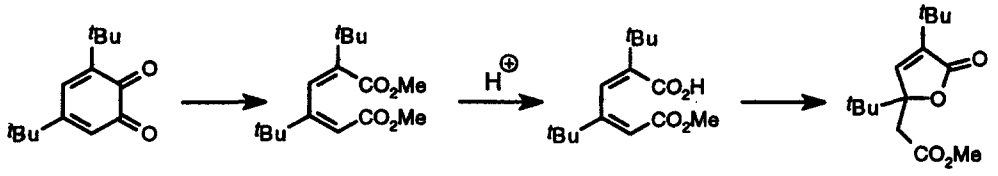
a $(PyCuClOMe)_2$: pyridine cupric methoxy chloride; CuClOMe: cupric methoxy chloride; pyr: pyridine; Py_2CuCl_2: bispyridine cupric chloride; [b] ref. 23; [c] ref 22; [d] 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (3,5-di-*tert*-butylmuconic anhydride);

Alternatively Speier and Tyeklar[23] reported that cupric methoxy chloride[27] (CuClOMe) anaerobically ring cleaved 3,5-di-*tert*-butyl-*o*-benzoquinone to generate the ring opened dimethyl 2,4-di-*tert*-butylmuconate. When we attempted this reaction under the same conditions however, we found that the predominant product isolated was not the diester but lactone **13** (entry 12). It should be noted that Speier

and Tyeklar[23] themselves had reported this same furanone as the product of the oxidative ring cleavage of 3,5-di-*tert*-butylcatechol *via* its quinone with copper(I) chloride in methanol and pyridine under an oxygen atmosphere.

Origin of lactones (13)/(15) and alternative work-ups.

The appearance of lactone **13** and chlorolactone **15** in this copper-based process was very reminiscent of the similar appearance of **13** in the analogous lead-based process (Scheme 3). Thus it is quite clear that the products of oxidative ring-opening of this substrate are prone to such conversion. In common with previous workers,[14,22,23] we attribute the lactones to hydrolysis of one ester moiety by adventitious acid to give the mono-ester which could then undergo lactonisation (Scheme 6). Such lactonisation is well-precedented for muconates.[19,21,26,28-30] It should be noted however that during this work it was only the 3,5-di-*t*-butyl catechol that was observed to give the analogous five-membered lactone as a product. For all the other substrates, no lactone formation was observed under similar reaction conditions. It could be speculated that the 3,5-di-*tert*-butyl-catechol is particularly prone to this side reaction due to the presence of the two bulky *t*-butyl groups enforcing a conformation that would favour lactone formation.



Scheme 6

A complication which attends the interpretation of the above work and indeed of all of the copper-related mechanistic work is the ubiquitous presence of strong hydrochloric acid in the work-up procedure. This may be contributing to the lactonisation and/or the chlorination of the lactones so an alternative series of work-up procedures was investigated. These included methods involving known sequestering agents such as the disodium salt of ethylenediaminetetraacetate (EDTA) and dimethylglyoxime (DMG). However the use of both of these resulted in product distribution similar to that found in the normal procedure. Another possibility investigated was the use of hydrogen sulphide in the hope of generating solid copper(II) sulphide. A black solid was indeed isolated but again when worked-up a brown liquid was found from which only chlorolactone **15** was isolated. Simple extraction with no acid and room temperature solvent removal were similarly ineffective.

Given the variability of product distribution, the lack of clarity in the understanding of the oxidative process combined and the cumbersome and delicate reaction and work-up procedures, we conclude that this copper-based oxidation cannot be adapted to a general ring-opening of catechols. Despite the great promise of the method from a selective and stereospecificity point of view it was reluctantly abandoned.

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EXPERIMENTAL SECTION

General. Elemental analyses were performed by the Microanalysis Department at University College Cork. Infra-red spectra were obtained as KBr discs or as a thin film between NaCl plates on a Perkin-Elmer 783 spectrophotometer. Mass spectra were obtained on an A.E.I. 30 instrument and on a Kratos Profile machine. Melting points were determined using a Reichart hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C N.M.R. spectra were recorded in deuteriochloroform using the Fourier transform mode on either a Brucker

AC80 or a Jeol GX270 spectrometer using tetramethylsilane (TMS) as an internal standard. In all ^{13}C spectra a 135 *DEPT* was carried out. Chemical shifts are reported as δ-values in ppm. Positive shifts are universally reported downfield from the standard.

Analytical T.L.C. was performed on commercial silica-coated aluminium sheets with a fluorescent indicator (Merck-Art.5554) or on neutral aluminium oxide-coated aluminium sheets with fluorescent indicator (Merck-Art.5550) with realisation by ultraviolet irradiation. Preparative chromatography was done on Flash grade silica gel supplied by Aldrich Fine Chemicals (cat. no. 22,719-6, 230-400 mesh) and neutral aluminium oxide (Aldrich cat. no. 19,997-4). The columns were pressurised using a fish pump which was found to be adequate for all diameters up to and including 4 cm.

Solvents were dried using recognised procedures[31]. Oxygen-free nitrogen (Irish Industrial Gases) was dried by passage through concentrated sulphuric acid and then sodium hydroxide pellets. All the chemicals used, unless otherwise stated, were purchased from Aldrich Fine Chemicals Company and used without further purification. The lead tetraacetate used for the ring cleavage step was sometimes freshly generated as was copper(I) chloride[32]. 3-methyl, 4-methyl and 3,5-di*tert*-butylquinones were generated from the corresponding catechols using manganese dioxide according to the procedure recorded by Wiessler.[8] 3,6-Dimorpholinomethylcatechol was made by the method of Caldwell and Thompson[33] using a Mannich base condensation reaction involving the use of catechol, morpholine, formalin and ethanol. The structure was initially assigned the incorrect 3,5-configuration but was later amended by Fields and co-workers[34]. 4,5-Dimethoxy-*o*-benzoquinone was generated according to the method of Itoh and co-workers[35] from the oxidation of unsubstituted catechol with sodium iodate in methanol.

1. Oxidative Ring Cleavage of Catechols/Quinones with Lead Tetraacetate.

Initially we employed a slightly modified version of the method of Wiessler[7,8] which we refer to below as procedure A. Subsequent more extensive modification lead to our preferred method referred to as procedure B. Since not all substrates were subjected to the preferred method, both methods are given in each case for comparison.

Grade of lead tetraacetate. CAUTION: Although LTA is not commonly flagged as especially dangerous[11,36], lead compounds are classic heavy metal poisons and lead(II) acetate is carcinogenic.[11] Therefore special precautions should be taken to avoid contact of any kind and to dispose of or recycle residues. LTA is commonly supplied moistened with glacial acetic acid or acetic anhydride to prevent decomposition due to adventitious water and thus some acetic acid is always present as supplied, especially in lower grade LTA. We have found that recrystallisation of the LTA just prior to its use gave much superior results and we believe that this is at least partly due to the removal of acetic acid. Our recrystallisation protocol is different from that previously described.[32] Thus just prior to use, the LTA (Aldrich 95%) was dissolved in almost boiling glacial acetic acid (10-15 ml/g) containing a little (2-3%) acetic anhydride, left to cool for 2 h, the colourless translucent needles filtered, washed with a minimum amount (1-2 ml/g) of petroleum spirits (40-60) and transferred immediately to a desiccator and dried under vacuum over KOH pellets for approx. 1 h. Recovery is typically over 80%.

It was also observed that the grade of the lead tetraacetate used was important in determining the ease of the work-up and hence indirectly the yield. If technical grade lead tetraacetate was used a black scum-like material always appeared during the aqueous washing of the ethereal layer and this proved tedious to remove. The addition of a few millilitres of ethylene glycol to the organic filtrate *before washing* alleviated the problem, with no scum appearing upon the addition of water. Alternatively if 99% grade lead tetraacetate was used, then no scum-like material appeared upon washing with water. The same proved true if recrystallised technical grade lead tetraacetate was used. This improved yields as less washings were required to ensure all traces of lead salts were removed.

Procedure A. A large round-bottomed flask, equipped with a stirrer and fitted with a pressure equalised dropping funnel, was charged with lead tetraacetate, usually in slight excess, and dry benzene/methanol (1:1). This solution was stirred and cooled to approximately 0°C in an ice/water bath. The catechol (0.5 equivalent) or quinone (1 equivalent) was dissolved in dry benzene/methanol (1:1) and placed in the dropping funnel. The catechol/quinone solution was added dropwise to the cooled, stirred lead tetraacetate

solution and then left stirring at room temperature for up to 48 h. It was found that if the substrate was added too quickly a very dark black colour developed and the resultant yield was low, especially in the catechol cases. Usually as catechol substrate was added, the mixture changed colour from grey/brown to the deep red colour of the quinone and after addition, with continued stirring, the red colour faded to a clear pale red hue. However, if it did not so fade, indicating the persistence of the quinone, more lead tetraacetate (1g per g of catechol) was added until the colour had faded.

In the usual work-up the reaction mixture was evaporated and the red/yellow semi-solid residue was treated with chloroform. The resultant white precipitate was filtered and the cloudy light red filtrate was washed (x3) with water and dried over $MgSO_4$. Removal of the solvent usually left a red tinged semi-viscous liquid which was subsequently purified by column chromatography on silica to give the product which in each case eluted first. These were yellow tinged liquids or off-white solids. The quinone was very often a contaminant which eluted second. In three cases other side-product(s) were also formed.

Preferred Procedure B. The previous procedure was improved in several respects. A slight excess of freshly recrystallised (see above) lead tetraacetate was used. It was found that this obviated the need for further addition of LTA to complete the reaction. Toluene was substituted for benzene as reaction solvent and in the work-up, ether was substituted for chloroform as extracting solvent. It was found that the addition of a few millilitres of ethylene glycol to the organic layer, *pre-washing*, was very effective in preventing deposition of a black scum-like material, probably lead oxide associated by-products, upon the addition of water. These modifications enabled the initial addition to be conducted at room temperature.

To a stirred suspension of lead tetraacetate (2.2 equivalents) in dry toluene/methanol (1:1, approx. 5 ml of solvent/g of $Pb(OAc)_4$) was added, dropwise, a solution of the catechol (1 equivalent) dissolved in toluene/methanol (1:1, approx. 8 ml/g of catechol). After 24 to 48 hours stirring (<30 m in the case of electron-withdrawing substituents), the solvents were evaporated and the solids resuspended in ether. The lead solids were filtered and ethylene glycol (2-3 ml) added to the filtrate which was then washed with water, saturated $NaHCO_3$ solution and with water again. After evaporation of the solvent, the crude oil was purified by column chromatography as in procedure A.

(a) Dimethyl (2*Z*,4*Z*)-hexa-2,4-diene-1,6-dioate (1). Procedure A. From catechol (2.2 g; 20 mmol) in benzene/methanol (80 ml) and lead tetraacetate (17.7 g; 40 mmol) in benzene/methanol (80 ml). The mixture became grey in colour initially and then darkened as the addition proceeded to finally yield a dark black/brown solution. After 16 h stirring further lead tetraacetate (2.0 g) was added to yield, after a further 24 h stirring, a red/brown solution. Work-up gave a dark brown/yellow tinted liquid which solidified on cooling. Column chromatography (diethyl ether) yielded a bright yellow tinged solid which was recrystallised slowly from diethyl ether to give a pale yellow tinted solid: 2.0 g (60%); m.p. = 72-73 °C (lit.[9]: 73 °C); δH: 3.75 (s, 6H, CO_2Me); 6.00 (dd, 2H, -CH=CH-, ^3J = 10.3 Hz, ^4J = 2.3 Hz); 7.91 (dd, 2H, -CH=CH-, ^3J = 10.3 Hz, ^4J = 2.3 Hz) ppm (in accord with lit.[37]). **Procedure B.** From catechol (10.0 g, 91 mmol) after recrystallisation from diethyl ether/hexane (1:1): 11.3 g (73%).

(b) Dimethyl (2*E*,4*Z*)-3-*tert*-butylhexa-2,4-diene-1,6-dioate (2). Procedure A. From 4-*tert*-butylcatechol (3.4 g; 20 mmol) in benzene/methanol (80 ml) and lead tetraacetate (17.9 g; 40.4 mmol) in benzene/methanol (100 ml). The deep red colour paled slowly over twenty-four hours but addition of further lead tetraacetate (c. 2.0 g) was necessary until there was no further change of colour. After 48 h the solution was worked-up and the red tinged crude product was purified by column chromatography (diethyl ether/pentane (2:3)) to give a yellow/orange liquid: 4.1 g (90%); δH: 1.15 (s, 9H, -t-butyl); 3.65 (s, 6H, $-CO_2CH_3$); 5.84 (d, 1H, -CH=CH-, ^4J = 1.9 Hz); 5.98 (d, 1H, -CH=CH-, ^3J = 12.3 Hz); 6.75 (dd, 1H, -CH=CH-, ^3J = 12.3 Hz, ^4J = 1.85 Hz) ppm (in accord with lit.[21]). **Procedure B.** From 4-*tert*-butylcatechol purified by chromatography as above (10.0 g, 60 mmol): 12.6 g (93%).

(c) Dimethyl (2*Z*,4*E*)-2,4-di-*tert*-butylhexa-2,4-diene-1,6-dioate (3). Procedure A. From 3,5-di-*tert*-butyl-*o*-benzoquinone (7.0 g; 32 mmol) in benzene/methanol (100 ml) and lead tetraacetate (15.8 g; 35.7 mmol) in benzene/methanol (150 ml). After 18 h a clear yellow, red tinged colour persisted. The crude product was purified by column chromatography (diethyl ether/pentane (2:3)) to give a pale yellow, orange

tinged liquid: 8.1 g (90%); δH: 1.13 (s, 9H, -t-butyl); 1.22 (s, 9H, -t-butyl); 3.61 (s, 3H, CO_2Me); 3.67 (s, 3H, CO_2Me); 5.75 (d, 1H, -CH=CH-, ^4J = 1.7 Hz); 6.25 (d, 1H, -CH=CH-, ^4J = 1.7 Hz) ppm (in accord with lit.[7]); δC: 29.6, 29.7 (-CH_3); 37.6, 38.2 (-C-); 51.1, 51.3 (-OCH_3); 116.4, 125.9, 144.8, 162.5 (-CH=CH-); 167.6, 169.6 (-CO-) ppm. **Procedure B with unrecrystallised LTA.** From 3,5-di-*tert*-butylcatechol (10 g, 45 mmol). Separation of the lactone side-product **13** which contaminated some but not all reactions was accomplished by storage of the crude product dissolved in hexane/diethyl ether (1:1) solution (approx. 40 ml/g) in a freezer (-20 °C) for 48 hours. The lactone crystallised as a white solid which was then removed by filtration and the filtrate evaporated to yield the diester: 8.9-12.1 g (70-95%) as a yellow oil. The lactone, methyl (2,4-di-*tert*-butyl-5-oxo-2,5-dihydro-furan-2-yl)acetate, was further purified by recrystallisation from hexane/diethyl ether (1:1): 0-2.9 g (0-25%); m.p.: 70-72 °C (lit.[22]: 68-69 °C); δH: 0.98 (s, 9H, -t-butyl); 1.24 (s, 9H, -t-butyl); 2.87 (ABq, 2H, -CH_2-); 3.59 (s, 3H, -OCH_3); 6.97 (s, 1H, -CH=CH-) ppm (in accord with lit.[22]). **Procedure B.** From 3,5-di-*tert*-butylcatechol (1 g, 4.5 mmol); 1.2 g, (95%).

(d) Dimethyl (2*Z*,4*Z*)-3-methylhexa-2,4-diene-1,6-dioate (4). Procedure A. From 4-methylcatechol (2.5 g; 20 mmol) in benzene/methanol (100 ml) and lead tetraacetate (17.7 g; 40 mmol) in benzene/methanol (160 ml). After 24 h stirring extra lead tetraacetate (c. 2.0 g) was added to generate a yellow/red tinted colour. The work-up yielded a clear pale orange liquid which was purified by column chromatography (diethyl ether/pentane (2:3)) giving an almost colourless, yellow tinged liquid: 1.4 g (39%); δH: 2.10 (s, 3H, -CH_3); 3.65 (s, 3H, CO_2Me); 3.75 (s, 3H, CO_2Me); 5.80 (s, 1H, -CH=CH-); 5.87 (d, 1H, -CH=CH-, ^3J = 12.0Hz); 7.14 (d, 1H, -CH=CH-, ^3J = 12.0 Hz) ppm (lit. ^{1}H-NMR[14]: see Table 2). **Procedure B.** From 4-methylcatechol purified by chromatography as above (10 g, 0.08 mole); 7.7 g (52%). From 4-methylcatechol (0.95 g; 7.8 mmol) yield estimated as 76% from ^{1}H NMR, remainder starting material.

(e) Dimethyl (2*Z*,4*Z*)-2-methylhexa-2,4-diene-1,6-dioate (5). Procedure A. From 3-methylcatechol (2.3 g; 19 mmol) in benzene/methanol (100 ml) and lead tetraacetate (17.7 g; 40 mmol) in benzene/methanol (160 ml). During addition the resultant solution became almost black in colour which persisted irrespective of the amount of lead tetraacetate used. After thirty hours stirring the solvent was removed to give a dark viscous semi-solid. This proved insoluble in chloroform but on addition of water it dissolved after vigorous shaking. The organic portion had to be washed vigorously with water (x5) which yielded a pale brown chloroform solution. Evaporation gave a crude dark red/brown liquid, the TLC analysis of which showed only one intense mobile spot and the absence of starting material. Purification by column chromatography (diethyl ether/pentane (2:3)) gave a clear yellow tinged fraction. This solidified to give a white solid which was recrystallised from diethyl ether/pentane (2:1): 1.8 g (50%); m.p.: 48-50 °C; Calc. for $C_9H_{12}O_4$: C, 58.68; H, 6.56; Found: C, 58.06; H, 6.45; ν_{max}: 2960, 1720 (-C=O), 1640, 1590, 1440, 1410, 1350, 1220, 1200, 1180, 1020, 900, 840, 770 cm^{-1}; δH: 2.07 (s, 3H, -CH_3); 3.74 (s, 3H, CO_2Me); 3.78 (s, 3H, CO_2Me); 5.82 (d, 1H, -CH=CH-, ^3J = 10.1 Hz); 7.37-7.69 (m, 2H, -CH=CH-) ppm; δC: 21.6 (-CH_3); 51.6, 52.2 (-OCH_3); 121.2, 133.4, 135.2, 140.0 (-CH=CH); 166.7, 167.8 (-CO-) ppm; m/z: 185 (0.5%, M^++1); 184 (6, M^+); 169 (2, M^+-CH_3); 153 (7, M^+-OCH_3); 126 (10, M^++1-CO_2CH_3); 125 (100, M^+-CO_2CH_3). **Procedure B.** From 3-methylcatechol (0.98 g; 8.1 mmol) yield estimated as 54% from ^{1}H NMR, remainder starting material.

(f) Dimethyl (2*E*,4*Z*)-2-methoxyhexa-2,4-diene-1,6-dioate (6). Procedure A. From 3-methoxycatechol (3.0 g; 21 mmol) in benzene/methanol (100 ml) and lead tetraacetate (17.7 g; 40 mmol) in benzene/methanol (120 ml). As the catechol was added a series of colour changes occurred, from initial yellow to orange to red to black which then persisted despite stirring for 24 h and the addition of some extra lead tetraacetate. Like the 3-methylcatechol case above, a dark brown chloroform solution was recovered which required successive washing with water (x6) to generate a dark orange solution. Again evaporation produced a crude dark brown/orange liquid which was purified by column chromatography (diethyl ether/pentane (2:3)) to yield one product, a white solid which was subsequently recrystallised from diethyl ether/pentane (2:1): 3.9 g (92%); m.p. 49-51 °C (lit.[38]: 48-49 °C); δH: 3.65 (s, 3H, CO_2Me); 3.70 (s, 3H, OMe); 3.77 (s, 3H, CO_2Me); 5.63 (d, 1H, -CH=CH-, ^3J = 10.1 Hz); 7.22-7.68 (m, 2H, -CH=CH-) ppm (in accord with lit.[38]); δC: 51.4, 52.7, 56.4 (-OCH_3); 107.6, 117.6, 139.7, 152.1 (-CH=CH-); 163.23, 167.5 (-CO-) ppm.

(g) Dimethyl (2Z,4Z)-2,3,4,5-tetrachlorohexa-2,4-diene-1,6-dioate (7). Procedure A. From tetrachloro-*o*-benzoquinone (2.5 g; 9.96 mmol) in benzene/methanol (170 ml) and lead tetraacetate (5.0 g; 11.3 mmol) in benzene/methanol (80 ml). This gave a clear yellow/brown solution after overnight stirring. After the usual work-up a dark yellow/brown liquid was recovered which was purified by column chromatography (diethyl ether/hexane (2:3)) to give a clear yellow liquid: 3.4 g (98%); b.pt. 92-94 °C @ 1 mmHg (lit.[39]: 105 @ 3 mmHg); Calc. for $C_8H_6O_4Cl_4$: C, 31.20; H, 1.96; Cl, 46.05; Found: C, 31.55; H, 2.18; Cl, 45.90; ν_{max}: 3000, 2980, 2840, 1730 (-C=O), 1610, 1560, 1430, 1260 (-C-O), 1060, 1030, 980, 920, 760, 730, 650 cm^{-1}; δH: 3.75 (s, 6H, CO_2Me) ppm; δC: 54.1 (-OCH_3); 126.8, 137.8 (-CH=CH-); 160.9 (-CO-) ppm; m/z: 307 (0.1%, M^+); 274 (40), 272 (100), 270 (100, M^+-Cl); 250 (14), 248 (27), 246 (22, M^+-CO_2CH_3); 191 (2), 189 (5), 187 (4, M^+-2xCO_2CH_3); 156 (6), 154 (13), 152 (13, M^+-Cl-2xCO_2CH_3); 121 (4), 119 (24), 118 (37, M^+-2xCl-2xCO_2CH_3); 86 (19), 84 (22), 82 (41, M^+-3xCl-2xCO_2CH_3); 59 (100, CO_2CH_3). **Procedure B.** From tetrachlorocatechol (10 g, 0.04 mole) purified *via* chromatography as above: 11.9 (96%).

(h) Dimethyl (2Z,4Z)-2,3,4,5-tetrabromohexa-2,4-diene-1,6-dioate (8). Procedure A. From tetrabromocatechol (2.1 g; 5 mmol) in benzene/methanol (60 ml) and lead tetraacetate (4.5 g; 10 mmol). After overnight stirring and usual work-up, a crude red liquid resulted which was purified by column chromatography (diethyl ether/hexane (2:3)) giving a red tinged liquid: 2.2 g (90%). **Procedure B.** From tetrabromocatechol purified by chromatography as above (2 g, 24 mmol): 2.2 g (95%); Calc. for $C_8H_6O_4Br_4$: C, 19.78; H, 1.24; Br, 65.79; Found: C, 20.08; H, 1.26; Br, 65.95; ν_{max}: 3000, 2950, 2840, 1730 (-C=O), 1600, 1540, 1430, 1250 (-C-O), 1030, 1000, 960, 890, 760, 700, 680 cm^{-1}; δH: 3.80(s, 6H, CO_2Me) ppm; δC: 54.4 (-OCH_3); 120.2, 133.7 (-CH=CH-), 161.7 (-CO-) ppm; m/z: 458 (0.3%), 456 (1), 454 (2), 452 (2, M+-OCH_3); 408 (35), 406 (100), 404 (99), 402 (35, M^+-Br); 349 (3), 347 (9), 345 (10), 343 (3, M^+-Br-2xOCH_3); 268 (6), 266 (12), 264 (6, M^+-2xBr-2xOCH_3); 209 (11), 207 (24), 205 (13, M^+-2xBr-2xCO_2CH_3); 132 (11), 130 (12), 128 (12), 126 (12, M^+-3xBr-2xCO_2CH_3); 81 (16), 79 (16, Br).

(i) Dimethyl (2Z,4Z)-2,5-bis(morpholin-4-ylmethyl)hexa-2,4-diene-1,6-dioate (9). Procedure A. From 3.6-dimorpholinomethylcatechol[33,34] (2.0 g; 6.5 mmol) in benzene/methanol (80 ml) and lead tetraacetate (6.0 g; 13.5 mmol) in benzene/methanol (100 ml). The reaction mixture became deep red in colour overnight. A further amount of lead tetraacetate (c. 2.0 g) was added which gave a clear orange/red solution after a further 24 h stirring. The usual work-up yielded an orange/red viscous liquid which partially solidified on cooling. The solid was triturated with diethyl ether and recrystallised from diethyl ether/hexane (3:1) to give an off-white solid. Alternatively purification by column chromatography (diethyl ether) slowly eluted a pale yellow tinted solid which was similarly recrystallised: 1.5 g (62%); m.p. 133-135°C; Calc. for $C_{16}H_{28}N_2O_6$: C, 58.68; H, 7.66; N, 7.60; Found: C, 58.51; H, 7.66; N, 7.57; ν_{max}: 2980, 2960, 2850, 2800, 1690 (-C=O), 1440, 1420, 1370, 1340, 1330, 1290, 1270, 1220, 1110, 1080, 1070, 1030, 1010, 940, 910, 860, 750 cm^{-1}; δH: 2.49 (m, 8H, -CH_2N-); 3.28 (s, 4H, -CH_2-); 3.72 (m, 8H, -CH_2O-); 3.83 (s, 6H -CO_2CH_3); 7.33 (s, 2H, -CH=CH-) ppm; δC: 52.0 (-OCH_3); 53.8 (-CH_2N-); 61.7 (-CH_2N); 67.2 (-CH_2O-); 133.7, 133.9 (-CH=CH-); 167.6 (-CO-) ppm; m/z: 369 (8%, M^++1); 283 (82, M^+-NCH_2CH_2O); 281 (58); 252 (15, M^++ 1 -NCH_2CH_2O-OCH_3); 222 (79, M^++1-NCH_2CH_2O- 2xOCH_3); 196 (20, M^+-2xNCH_2CH_2O); 137 (28, M^+-2x $CH_2NCH_2CH_2O$-OCH_3); 100 (90, $CH_2NCH_2CH_2O$); 86 (100, NCH_2CH_2O); 59 (14); 57 (31).

(j) Methyl Z-*o*-carbomethoxycinnamate (10). Procedure B. From 1,2-naphthoquinone (1.0 g; 63 mmol) in dry toluene/methanol (8 ml) and lead tetraacetate (3.1 g; 70 mmol) in dry toluene/methanol (15 ml). The reaction mixture became deep red upon addition of the quinone and paled quickly to an orange/pink colour. After overnight stirring the usual workup yielded an orange oil 1.3 g (96%); Calc for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49; Found: C, 65.43; H, 5.46; δH: 3.58 (s, 3H, -OCH_3); 3.87 (s, 3H, -OCH_3); 6.04 (d, 1H, CH=CH; J = 12.1 Hz); 7.57 (d, 1H, CH=CH; J = 12.1 Hz) ppm (in accord with lit.[40]); δC: 51.6 (-OCH_3); 52.0 (-OCH_3); 119.0 (-CH=CH-); 128.0 (-C-); 128.1, 130.2, 131.8 (Ar with an apparent peak coincidence); 138.1 (-C-); 145.5 (-CH=CH-); 166.3, 166.9 (-CO-); m/e: 220 (3%, M^+); 205 (1, M^+-Me); 189 (10, M^+-OMe); 173 (20); 162 (21); 161 (100, M^+-CO_2Me).

(k) Dimethyl (2*E*,4*Z*)-3-nitrohexa-2,4-diene-1,6-dioate (11). Procedure A. From 4-nitrocatechol (1.3 g; 8.4 mmol) in benzene/methanol (50 ml) and lead tetraacetate (8.5 g; 19.1 mmol) in benzene/methanol (100 ml). After stirring for 24 h the solution was a bright red/orange colour. Evaporation left an orange semi-solid from which an orange coloured solid and orange/yellow filtrate were isolated after the normal work-up. After washing with water (x3), drying with $MgSO_4$ and evaporation, a brown/orange crude liquid was recovered. NMR analysis of this crude material showed the presence of two related diester type compounds which were purified but not separated by column chromatography (diethyl ether/pentane (2:3)). The relative proportions of these compounds varied on different runs and despite many TLC analyses with various solvents it proved impossible to achieve adequate separation of these two products: 1.7 g (crude) (91%): *Compound A*: has the characteristics expected for the desired compound (**11**): δH: 3.64 (s, 3H, -OCH_3); 3.92 (s, 3H, -OCH_3); 6.35 (s, 1H, -CH=CH-); 6.71 (d, 1H, -CH=CH-, ^3J = 7.0 Hz); 7.67 (d, 1H, -CH=CH-, ^3J = 7.0 Hz) ppm. *Compound B*: is presently unidentified (see discussion): δH: 3.48 (s, 3H,- OCH_3); 3.93 (s, 3H, -OCH_3); 6.52 (d, 1H, -CH=CH-, J = 7.06 Hz); 7.80 (d, 1H, -CH=CH-, J = 7.06 Hz) ppm.

(l) Attempted preparation of dimethyl (2*E*,4*E*)-3,4-dimethoxyhexa-2,4-diene-1,6-dioate (12). 4,5-Dimethoxy-*o*-benzoquinone[35] (0.4 g; 2.4 mmol) in benzene/methanol (30 ml) was added dropwise to a stirred solution of lead tetraacetate (1.2 g; 2.7 mmol) in benzene/methanol (30 ml) to give a dark brown solution. After overnight stirring the red colour persisted and more lead tetraacetate (c. 2.0 g) was added giving an orange coloured solution. After the usual work-up a dark orange solid (0.30 g, crude) was isolated. Since NMR and TLC analysis showed the presence of at least four products in apparently equal amounts this preparation was not pursued further.

(m) Attempted ring cleavage of 2,3 -dihydroxynaphthalene. 2,3-Dihydroxynaphthalene (1.6 g; 10 mmol) was dissolved in benzene/methanol (50 ml) and added dropwise to a solution of lead tetraacetate (9.0 g; 20 mmol) in benzene/methanol (100 ml). This gave a pale yellow solution which was stirred overnight. After the usual work-up a small amount of yellow viscous oil (0.28 g, crude) was recovered. Since TLC analysis showed a large number of products, no attempt was made to isolate them and the reaction was abandoned.

2. Oxidation of catechols and quinones using copper(I) based oxidising systems.

(a) Copper(I) chloride/pyridine/methanol/catechol.[9] Freshly prepared copper(I) chloride (9.0 g; 91 mmol) was added to a stirred solution of dry pyridine (182 ml) and dry methanol (4.5 ml; 0.1 mol) under an atmosphere of dry nitrogen. Then oxygen was slowly bubbled through the resultant bright yellow solution for two hours generating a dark green viscous solution. The catechol (5.0 g; 45.5 mmol), dissolved in dry pyridine (92 ml) and dry methanol (4.5 ml; 0.1 mol), was added very slowly to the vigorously stirred green solution while oxygen was being slowly bubbled through the mixture. It was found that slow addition was necessary for the maintenance of the dark green colour which presaged a good yield, otherwise a black coloured solution was produced associated with a greatly diminished yield. After addition was complete the solvent was evaporated from the green solution giving a dark green mass which was treated with hydrochloric acid (6N, 200 ml) and dichloromethane (200 ml) with filtration of any remaining insoluble material. The two layers which were both dark brown in colour proved difficult to separate. However, once separated, the aqueous layer was further washed with dichloromethane (x3), the organic layer and washings were combined, dried over $MgSO_4$ and evaporated. The products of the reaction were then isolated from the residue by extraction with hot hexane giving a clear yellow-tinged liquid which on cooling produced a white fibrous solid which was recrystallised from hexane. This compound was characterised as the expected product, monomethyl muconic acid **14**: 5.3 g (75%); m.p. 76-77 °C (lit.[9]: 80 °C.); δH: 4.15 (s, 3H, -OCH_3); 6.30-6.35 (m, 2H, -CH=CH-); 8.25-8.60 (m, 2H, -CH=CH-); 12.40 (s, 1H, -OH) ppm (in accord with lit.[9]); δC: 52.4 (-CH_3); 125.1, 126.1, 139.0, 139.1 (-CH=CH-); 167.2, 1 67.8 (-C=O) ppm.

(b) Copper(I)chloride/pyridine/methanol/3,5-di-*tert*-butylcatechol. Freshly prepared copper(I) chloride (7.2 g; 73 mmol) was stirred under dry nitrogen in a mixture of dry pyridine (146 ml) and dry methanol (3.65 ml; 0.14 mol). Oxygen was then bubbled through this yellow solution and after two hours a deep green coloured solution had resulted. 3,5-Di-*tert*-butylcatechol (8.0 g; 36 mmol) in dry pyridine (73 ml) and

dry methanol (3.65 ml; 0.14 mol) was then added slowly maintaining the deep green colour. After the removal of solvent and with hydrochloric acid (6N, 200 ml) and dichloromethane (200 ml) two layers remained, a pale blue aqueous and a green organic. The latter layer was reduced to a small amount of a dark oily liquid from which a small amount of white solid was isolated. This solid was fully characterised and identified as one diastereomer of chlorolactone **15**, methyl (2,4-di-*tert*-butyl-5-oxo-2,5-dihydro-furan-2-yl)chloroacetate: 1.6 g (15%); m.p. 104-107 °C (lit.[22]: 105-106 °C); Calc. for $C_{15}H_{23}O_4Cl$: C, 59.50; H, 7.65; Cl, 11.70; Found: C, 59.80; H, 7.77; Cl, 11.69; ν_{max}: 3005, 2960, 2860, 1770, 1760 (C=O), 1740, 1735 (C=O), 1480, 1465, 1430, 1370, 1360, 1350, 1310, 1280, 1250, 1220, 1190, 1160, 1110, 1090, 1040, 1020, 1000, 990, 880, 860, 790, 780, 730, 710, 650 cm^{-1}; δH: 1.01 (s, 9H, -t-butyl); 1.30 (s, 9H, -t-butyl); 3.82 (s, 3H, $-OCH_3$); 4.84 (s, 1H, -CHClCO-); 7.20 (s, 1H, -CH=C-) ppm (in accord with lit.[22] except for signal at 1.01 ppm); δC: 26.5, 28.6 ($-CH_3$); 32.4, 38.5 (-C-); 53.7 ($-OCH_3$); 59.3 (-CHCl-); 89.5 (-C-); 143.1 (-C=); 146.7 (CH=C-); 168.7 (-COO-); 170.9 (-C=O) ppm; m/z: 305 (24, M^++2); 304 (12, M^++1); 303 (63, M^+); 248 (20, M^++2-t-butyl); 246 (58, M^+-t-butyl); 231 (M^+-t-Butyl-CH_3); 211 (100, M^+-t-butyl-Cl); 195 (41, M^+-$CHClCO_2CH_3$); 57 (78, -t-butyl).

The solvent was removed from the blue aqueous layer to leave a green/orange crystalline residue. On drying this solid (11.0 g) became orange in colour and had an odour of pyridine. This product proved to be insoluble in most dry organic solvents except dimethylformamide at room temperature. It was soluble in hot acetone and ethanol and turned green in hot tetrahydrofuran. The compound turned blue in water and had a high conductivity value. It also gave a white precipitate with a solution of sodium tetraphenylborate. These observations indicated the presence of an inorganic copper salt whose structure was confirmed by comparative infra-red spectroscopy as bispyridinium tetrachlorocuprate, $(C_5H_5NH^+)_2(CuCl_4)$. This structure was authenticated by comparison with a sample made by the method of Wolf and Henning[41]. During a number of attempts at this oxidation, varying amounts of small bright blue crystals were recovered from the work-up procedure. These were dried, analysed and identified as a known side product of this reaction system, namely bispyridine cupric chloride[19].

(c) Use of pre-made copper complexes for ring cleavage of 3,5-di-*tert*-butylcatechol/quinone. Instead of generating the active oxidative species *in situ* as in *(a)* and *(b)* above, attempts were made to use various copper complexes which would mimic the action of the active copper species. It was also hoped that this might also give an insight into the mechanism of the reaction.

(i) $PyCuClOCH_3$ with catechol in dichloromethane and methanol. This complex was made by the method described by Hay *et al*[27] from sodium methoxide, anhydrous copper(II) chloride, dry methanol and dry pyridine. The dark green solid was dried and then immediately used in the oxidation. The complex (1.0 g; 4.8 mmol) was added to dichloromethane (60 ml) containing dry methanol (5 ml) while oxygen was being bubbled through it to generate a dark yellow/green solution. To this stirred mixture 3,5-di-*tert*-butylcatechol (2.2 g; 9.9 mmol) in dichloromethane (40 ml) was added dropwise with oxygen still bubbling through the system. After 2 h the reaction mixture was red in colour with green solid present. After further overnight bubbling of oxygen the green solid was filtered and the red filtrate reduced to a red liquid from which dark red crystals of 3,5-di-*tert*-butyl-*o*-benzoquinone were isolated: 1.4 g (64%).

(ii) $PyCuClOCH_3$ with catechol in pyridine and methanol. The complex (0.55 g; 2.6 mmol) was stirred in a mixture of dry pyridine (35 ml) and dry methanol (5 ml) with oxygen bubbling through the mixture. After two hours a solution of 3,5-di-*tert*-butylcatechol (1.5 g; 6.8 mmol) in pyridine (15 ml) and methanol (2 ml) was added dropwise. This resulted in the formation of a yellow/green solution. After 4 h the solvent was evaporated to leave a dark green/red semi-solid. This was treated with dilute hydrochloric acid (20 ml) and dichloromethane (20 ml) to give two layers; a pale green aqueous and a dark red organic. The latter was reduced to a red solid, 3,5-di-*tert*-butyl-*o*-benzoquinone: 1.3 g (86%).

(iii) $PyCuClOCH_3$ and Py_2CuCl_2 with catechol in pyridine and methanol. Bispyridine cupric chloride is a known side product of copper(I)chloride/pyridine/methanol oxidation system as shown in *(b)* above so it was added to $PyCuClOCH_3$ in an attempt to generate oxidative ring cleavage. The complex, (0.25 g; 1.2 mmol) and bispyridine cupric chloride (0.25 g; 0.85 mmol) were added to a stirred mixture of dry pyridine (20 ml) and dry methanol (4 ml) and oxygen was bubbled through the system. To this mixture was added dropwise a solution of 3,5-di-*tert*-butylcatechol (1.0 g; 4.5 mmol) in pyridine (10

ml) and methanol (2 ml). After addition oxygen was bubbled through for 2 h giving a green/red solution. The usual work-up procedure was applied and a red solid was isolated from the organic layer, namely, 3,5-di-*tert*-butyl-*o*-benzoquinone: 0.81 g (82%).

(iv) $PyCuClOCH_3$ with quinone in pyridine and methanol. The same procedure as employed in (ii) above was used with the same quantities of the respective reagents. The product recovered from the organic layer was characterised as unreacted starting material, 3,5-di-*tert*-butyl-*o*-benzoquinone: 1.45 g (97%).

(v) $PyCuClOCH_3$ and Py_2CuCl_2 with quinone in pyridine and methanol. The same procedure and amounts of reagents were employed as in (iii). A red solid was isolated from the reaction mixture and characterised as starting material, 3,5-di-*tert*-butyl-*o*-benzoquinone: 0.92 g (92%).

(vi) $CuClOCH_3$ with quinone in pyridine. The complex (2.9 g; 0.22 mmol), made by the action of sodium on methanol in the presence of anhydrous copper(II) chloride[42], was stirred under nitrogen in dry pyridine (60 ml). To this mixture 3,5-di-*tert*-butyl-*o*-benzoquinone (1.2 g; 5.4 mmol) was added. The resultant solution was stirred under nitrogen for 24 h. The reaction mixture was red/brown in colour with a brown solid present. The solvent was then evaporated and the dark brown semi-solid was treated with dichloromethane and water. This gave two layers both brown in colour with some undissolved brown solid. A small amount of dilute hydrochloric acid was then added and the mixture was shaken resulting in a pale blue aqueous layer and a red/brown organic layer. The latter was separated, filtered and the solvent evaporated to give a red solution. NMR and TLC analysis showed the presence of three products, one of which was starting quinone. From this mixture a white solid, the predominant product, was isolated by treating with hexane. This solid was characterised and determined to be the lactone **13**: 0.83 g (57%), previously characterised in 1(c).

(d) Work-up variations in the copper(I) chloride/pyridine/methanol/3,5-di-*tert*-butyl catechol system. In an attempt to increase the yield in this system, the viscous green copper(I)chloride/pyridine/methanol solution was prepared as outlined above in *(b)* using the same quantities with the solution of 3,5-di-*tert*-butylcatechol in pyridine/methanol added slowly maintaining the dark green colour. After oxygen was bubbled through for 2 h, the reaction mixture was split into 20 ml portions and various different work-up procedures were then applied:

(i) Using water instead of acid. After the solvents were removed under reduced pressure the dark green residue was treated with dichloromethane and water. This gave a cloudy pale green organic layer which was filtered to remove some insoluble salts. The clear green filtrate was reduced to a blue/green solid which was treated with hot hexane. The dark brown hexane washings were reduced to a brown oil similar to that obtained in 2(b).

(ii) Using disodium ethylenediaminetetraacetate. After the evaporation of solvent the dark green residue was treated with dichloromethane (100 ml) and an aqueous solution (0.1M) of EDTA (disodium salt) (100 ml)[43]. This gave two layers; an electric blue aqueous layer and a pale yellow/green organic layer. The latter was dried and reduced to a clear brown oily liquid. NMR analysis showed this to be similar to the liquids isolated previously.

(iii) Using dimethylglyoxime. The pyridine/methanol was evaporated and the residue treated with an acetone solution of excess dimethylglyoxime and left stirring for about a half hour. It was allowed to settle and some green solid precipitated. This was removed by filtration and the acetone evaporated to a give black semi-solid. This was treated with hot hexane and the extract was reduced to a dark brown/black liquid. NMR analysis showed the presence of many compounds.

(iv) Using hydrogen sulphide gas. Again the solvents were evaporated and the green residue was slurried in dichloromethane. The green insoluble portion was removed by filtration and the green dichloromethane solution was treated with hydrogen sulphide gas from a Kipp's apparatus[43] for 15 m causing a colour change from green to black. The solution was allowed to settle and precipitated a black solid leaving a clear yellow/brown dichloromethane layer. Nitrogen gas was bubbled through the solution to drive off residual hydrogen sulphide. The solvent was then removed leaving a clear yellow liquid which again had a complex NMR spectrum. A small amount of white solid precipitated from solution and analysis showed this to be chlorolactone **15**, previously characterised in 2(b).

(v) Removal of solvent without heat. The green mixture was rendered solvent free by reduced pressure removal of the pyridine and methanol to give a green solid. This solid was divided into two batches.

The first batch was worked-up in the usual manner using hydrochloric acid generating the same products as in 2(b). The second batch was treated with EDTA (disodium salt) in a manner similar to (ii) above. The organic layer yielded a brown oily product similar to that found in the other work-ups.

Overall only a small yield of product was found despite the various work-up processes applied. Irrespective of the type of work-up procedure involved the same oily mixture was recovered from which a small amount of white solid could be isolated. At no time was the anticipated product, the muconic monomethyl ester detected.

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