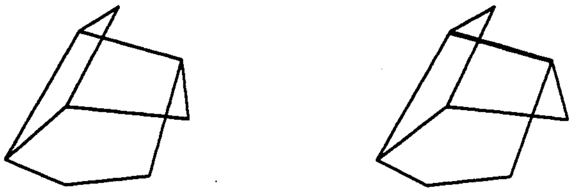

Figure 25. Stereoview of the unprojection of a complicated drawing.

4. Macrocyclic ring projections have their own logic, the basic conformational and pictorial rules for which have been enumerated by Dale.[29] Unprojection of these is not addressed by ZED. The basic rule for construction of these projections seems to be to connect runs of *all-anti*-butane units oriented in various ways. Unprojection will proceed in this way also. The iconic nature of conformational pictures is apparent when we consider the two different molecules shown (monoscopic view) in Figure 24. The bottom picture is derived from the top by simply addition of two carbons to the back *anti*-butane run; otherwise they are identical.

In summary, the curious fact about iconic projections as illustrated above is that, because they are *representations*, the fact that they are not projections at all is immaterial for most purposes. One merely has to learn the rules for interpreting them!

Conclusions. Machine recognition of conformational pictures is possible. The problem is complicated by several features, foremost of which is the iconic nature of some structural diagrams. This iconic aspect of structural diagrams and, indeed, structural formula in general, was noted by Sir Robert Robinson as early as 1917.[1] Secondly, it is useful to classify the various graphics objects associated with stereochemical pictures of organic molecules into two groups: those (Wedge, etc.) that impose a spatial ordering on *atoms* and those (Fat bond, etc.) that impose a spatial ordering on *bonds*. These are fundamentally different marks. Thirdly, a simple program (ZED) is described that is remarkably successful in interpreting these pictures. It succeeds in many cases by proceeding in a manner that is, frankly, surprising. Our favorite example of unexpected success is a drawing of bicyclo[3.3.0.0^{2,6}]octane, taken from ref 27. Unprojection affords the stereoview as illustrated in Figure 25.

Supplementary Material Available: The program ZED (47 pages). Ordering information is given on any current masthead page.

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(28) Corey, E. J.; Feiner, N. F. *J. Org. Chem.* **1980**, *45*, 757–764.

(29) Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1115–1129, 1130–1148, 1149–1158.

Electroorganic Reactions. 38. Mechanism of Electrooxidative Cleavage of Lignin Model Dimers

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The mechanisms for oxidative cleavage of several phenolic ethers, models for lignins, have been investigated by a detailed comparison of the result of anodic oxidation at nickel anodes in alkaline electrolyte with that of oxidation in acetonitrile in the presence of a triarylamine redox catalyst. The latter reaction is unambiguously initiated by single-electron transfer (SET), and in this case the major product of cleavage is aldehyde (vanillin or syringaldehyde derivatives). At nickel anodes polymerization is predominant although the aldehydes are formed together with larger amounts of the corresponding carboxylic acids. Combinations of 4-hydroxyl, α-keto, β-*O*-aryl, and β-hydroxymethyl functionality are shown to be crucial for the oxidation at nickel; the carboxylic acid formation probably involves a route with initial hydrogen atom abstraction at the surface. Important chemical conversions precede and accompany oxidation in alkaline media, and these are associated with the propensity for polymerization.

Lignins are three-dimensional biopolymers comprised of oxygenated phenylpropane units[1] (Figure 1). Their oxidative degradation to useful low molecular weight aromatic compounds such as vanillin and syringaldehyde has been much studied and is commercially important. Degradation is achieved typically by oxidation with nitro aromatics,[2] air in alkaline solution at high temperatures,[3] electrochemical oxidation,[4] and a combined nitro aromatic/electrochemical oxidation.[5] Fungal degradation of lignin is also oxidative,[6] and one of the relevant enzymes, ligninase, is able to oxidize relatively simple lignin models.[7] The key reaction is cleavage of C_α–C_β bonds (Figure 1), and this reaction may involve electron transfer in at least some of the above-described processes. However, the mechanisms for such oxidative cleavages are poorly understood. This paper attempts to elucidate the mechanism of electrochemical degradation at nickel anodes in strongly alkaline solution. This process has many of the features of other, commercially used, methods, and the conclusions should have considerable general value. Product profiles

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[†] Brazil.

[‡] United Kingdom.

(1) Feugel, D.; Wegener, G. *Wood Chemistry, Ultrastructure, Reactions*; Walter de Guyter & Co.: Berlin, 1984; Chapter 6.

(2) Chum, H. L.; Baizer, M. M. *The Electrochemistry of Biomass and Derived Materials*; ACS Monograph 183; American Chemical Society: Washington, 1985; p 244.

(3) Othmer, K. *Encyclopedia of Chemical Technology*; 3rd ed.; J. Wiley & Sons: New York, 1983; Vol. 23, p 704 (709).

(4) (a) Utley, J. H. P.; Smith, C. Z. U.S. Patent No. 4786382 (22 November 1988); *European Patent No.* 0245418 (11 April 1990). (b) Chen, C. S.; Tien, L. L.; Yoshiyama, A.; Nonaka, T.; Chou, T. C. *Denki Kagaku* **1989**, *57*, 806; *Chem. Abstr.* **1989**, *111*, 136266j.

(5) Smith, C. Z.; Utley, J. H. P.; Petrescu, M.; Viertler, H. *J. Applied Electrochem.* **1989**, *19*, 535.

(6) Umezawa, T. *Wood Res.* **1988**, *75*, 21.

(7) (a) Labat, G.; Meunier, B. *J. Org. Chem.* **1989**, *54*, 5008. (b) *New J. Chem.* **1989**, *13*, 801.

0022-3263/91/1956-7305$02.50/0

Table I. Electrochemical Oxidation at Nickel of Lignin Model Dimers[a]

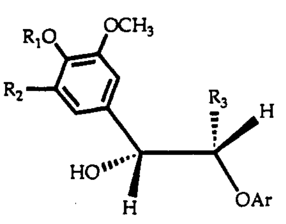
			cleavage products (%)[c]				
entry	compd	electrolyte[b]	aldehyde (3)	acid (4a)	guaiacol (5)	recovd starting material (%)	material balance (%)
1	**1a**	A	–	–	–	>95	>95
2	**1c**	A	–	–	–	>95	>95
3	**1d**	B	6.0 (**3a**)	–	7.5	55	68.5
4	**1e**	B	6.5 (**3a**)	–	8.5	0	15[d]
5	**1f**	B	9.0 (**3d**)	–	14	0	23[d]
6	**1g**	B	5.9 (**3b**)	15	4.0	18	42.9[e]
7	**2a**	A	–	20.9	25.4	0	24.3[f]
8	**2c**	A	–	40	<1	54	94[g]

[a] Stainless steel cell equipped with PTFE liner (volume 40 cm^3), Ni gauze cylinder anode (30 cm^2, 40 mesh), concentric stainless steel cylinders cathodes, heated to 150–160 °C; charge 6 F mol^{-1}; current 50 mA; substrate concentration 14–16 mM. [b] A: 1.5 M NaOH in H_2O/t-BuOH (1:1 v/v) (20 cm^3). B: 2.0 M NaOH in H_2O (20 cm^3). [c] Analyzed by HPLC with detector calibrated using mixtures of authentic samples and calculated based on starting material. [d] Much polymerization. [e] Trace amount of aldehyde **3a**, acid **4b**, and 3,4-dimethoxyacetophenone (<1%). [f] 3,4-Dimethoxyacetophenone (7.1%), acid **4b** <1%. [g] Acid **4b** <1%.

obtained from electrochemical oxidation of several lignin model dimers have been examined in an attempt to identify those structural features required for cleavage. The pattern of reactivity found is compared with that for oxidative cleavage, which is unambiguously initiated by electron transfer, i.e. electrolysis in the presence of the single-electron-transfer redox catalyst (mediator), tris(4-bromophenyl)amine.

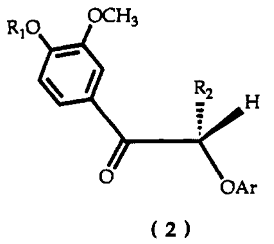
Results and Discussion

Model Compounds. The key compounds used in this study are **1a–j** and **2a–c**, where **1f**, **1h**, and **1j** are novel compounds (see the Experimental Section). Important structural features likely to have significant roles in the electrooxidative degradation are (i) the β-O-4-aryl ether linkage; (ii) the 4-methoxyl or 4-hydroxyl functions, and (iii) the substituents vicinal to the β-O-4-aryl function, i.e. at the α- and γ-positions (see Figure 1).



(**1**), usually erythro or erythro-rich
[Ar = 2-methoxyphenyl]

	R_1	R_2	R_3
a	CH_3	H	H
b	CH_2Ph	H	H
c	CH_3	H	CH_3
d	H	H	H
e	H	H	CH_2OH
f	H	OCH_3	CH_2OH
g	CH_3	H	CH_2OH
h	CH_3	H	$CO_2CH_2CH_3$
i	CH_2Ph	H	$CO_2CH_2CH_3$
j	CH_2Ph	OCH_3	$CO_2CH_2CH_3$



(**2**)

	R_1	R_2
a	CH_3	H
b	CH_2Ph	H
c	CH_3	CH_3

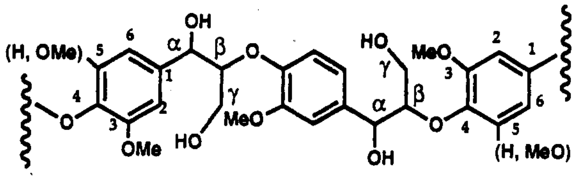
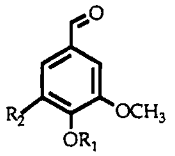


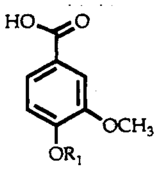
Figure 1. Key structural features and functionality of lignins.

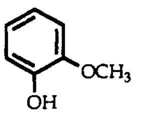
Electrooxidation. The lignin model compounds were oxidized amperostatically in a 1.5 M NaOH solution [H_2O–t-BuOH (1:1 v/v)], or 2 M aqueous NaOH, at a Ni gauze anode in a specially designed autoclave electrochemical cell.[5] This was heated at 150–160 °C for 1 h before and then throughout the electrochemical experiment. After the passage of the appropriate amount of electricity (usually 6 F mol^{-1}) the cell contents were worked up after neutralization and the lower molecular weight products analyzed for by HPLC. In some cases alkaline pretreatment prior to electrolysis was significant. This was identified by heating the reaction mixtures, without electrolysis, in the same cell. The results of the electrochemical experiments are displayed in Table I.

It is significant that compounds **1a**, **1d**, and **1g** were recovered unchanged when electrolyzed at room temperature without pretreatment, in an undivided cell equipped with nickel foil electrodes under otherwise the same experimental conditions as in Table I.



(3)	a	b	c	d	e
R_1	H	CH_3	CH_2Ph	H	CH_2Ph
R_2	H	H	H	OCH_3	OCH_3



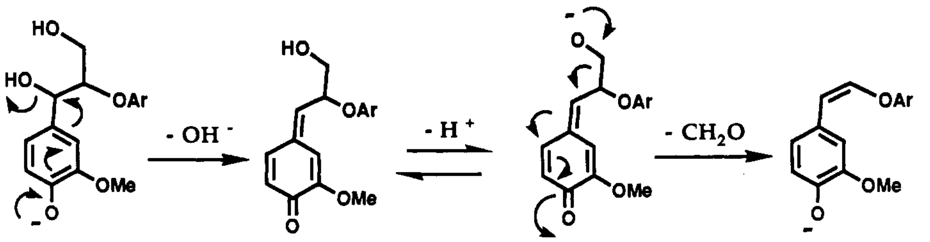


(4)	a	b
R_1	CH_3	H

(5)

Important Chemical Conversions. It is well established[8] that several important changes occur just by

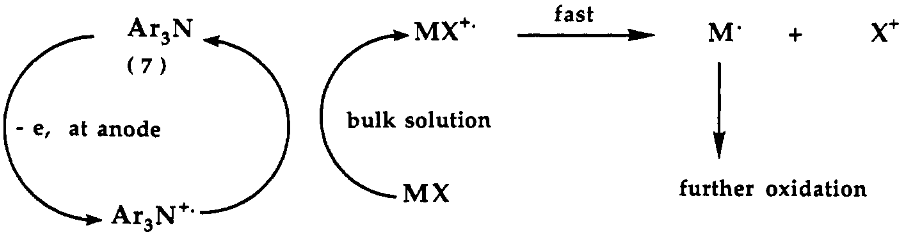
Scheme I



(1e) Ar = 2-methoxyphenyl

(6) + *trans* isomer

Scheme II



heating lignin model compounds in aqueous NaOH solution at temperatures above 150 °C. Especially important are those involving quinonemethide intermediates,[8b] e.g. Scheme I.

In this work such changes were observed for compounds **1e** and **1f**, Table I, entries 4 and 5. Thus **1e** when heated to 160 °C afforded vanillin (**3a**) (4.8%) and the enol ether **6** (ca. 70%) with a 1.1:1 cis/trans ratio according to the ^{1}H NMR spectrum. This enol ether is stable in alkaline solution but decomposes readily in neutral or acidic medium.[8b] In contrast a significantly different result was obtained with compound **1f**. The major cleavage products observed in this case were syringaldehyde (**3d**) (16%) and guaiacol (**5**) (51%), which agrees with the results described for a similar compound.[9] The 4-hydroxyl function is a common structural feature for compounds **1e** and **1f**, and this should favor formation of a quinone methide intermediate. To verify this assumption **1g**, which is 4-methoxyl substituted, was heated in alkaline solution under the same conditions and, as expected, it was recovered unchanged, almost quantitatively.

In view of these results the electrolysis of the enol ether **6**, confirmed in this study as formed chemically in alkali from 4-hydroxylated models, was examined both separately and also in the presence of the 4-methoxylated model **1g**. Because the enol ether **6** is only stable in alkaline solution it was generated in situ by heating **1e** for 1 h in the alkaline electrolyte and subsequently electrolyzed (6 F mol^{-1}) without prior isolation. The analysis of the reaction mixture by HPLC revealed vanillin (6.5%) as the only low molecular weight product; neither **6** nor **1e** was recovered, and extensive polymerization occurred. When a 1:1 mixture of **1e** and **1g** was preheated for 2 h followed by electrolysis (6 F mol^{-1}), a polymeric material, $(C_{10}H_{15}O_{24})_n$ by microanalysis, was isolated. This was insoluble in organic solvents which precluded its examination by gel-permeation chromatography. Its IR spectrum as well as the ^{1}H and ^{13}C NMR spectra of its peracetylated derivative revealed major structural changes with respect to the starting materials; specifically the material contained much carboxylic functionality, a relatively low level of methoxylation, and significant vinylic features. No polymeric material was observed when **1e** and **1g** were heated separately, and the electrolysis of **1g** afforded several cleavage products (Table I, entry 6).

Electrochemical Conversions. All compounds with a 4-hydroxyl group (Table I, entries 3–5) gave, after electrolysis, essentially similar yields of cleavage products. It seems reasonable to assume that in case of **1e** and **1f** (Table I, entries 4 and 5) the charge passed during electrolysis was used for the oxidation of the products formed by heating the substrates in alkaline solution. In both cases no starting material was recovered and extensive polymerization was observed. With compound **1d** (Table I, entry 3) the thermal reaction is less important (55% recovered starting material) but the cleavage products, **3a** and **5**, might have originated due to a partial alkaline degradation[8b] of **1d** as observed with **1e** and **1**.

When 4-hydroxyl is replaced by 4-methoxyl (**1a**, **1c**, and **1g**, Table I entries 1, 2, and 6) the alkaline degradation is not observed and therefore interpretation of the electrochemical experiments is less ambiguous. No oxidation was observed with **1a** and **1c** (entries 1 and 2), the starting materials being recovered. Electrooxidation of **1g** afforded **3b**, **4a**, and **5**, which must be due to an electrochemical cleavage reaction. The existence of an hydroxymethyl group at C_γ in **1g** seems to be the structural difference responsible for this distinctive behavior.

Replacing the C_α-hydroxyl function by carbonyl in compounds which otherwise did not cleave (**2a** and **2c**, Table I, entries 7 and 8) was observed to cause electrooxidative cleavage. The more efficient conversion process was observed for **2c**. There is a significant difference in products from **2a** and **2c**; the former gave the carboxylic acid **4a** (20.9%) and the phenol **5** (25.4%) whereas the latter gave only **4a** (40%). There is no obvious explanation of why replacing a C_β-hydrogen in **2a** by a methyl group causes such different behavior.

Mediated Electrolysis.[10] Indirect electrochemical processes combine an electrochemical and therefore heterogeneous electron-transfer reaction with a homogeneous redox process. The redox agent (mediator), in our case tris(4-bromphenyl)amine (**7**), reacts with the substrate in a homogeneous reaction and is subsequently regenerated

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[8] (a) Gierer, J.; Imsgard, F.; Pettersson, I. *Applied Polymer Symposium*, No. 28; John Wiley & Sons, Inc.: New York, 1976; p 1195. (b) Gierer, J.; Noren, I. *Acta Chem. Scand.* **1962**, *B16*, 1713.

[9] Miksche, G. E. *Acta Chem. Scand.* **1973**, *B27*, 1355.

[10] Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 683; *Top. Curr. Chem.* **1987**, *142*, 3.

Table II. Oxidation Peak Potentials of Lignin Model Dimers[a]

compd	$E_p{}^1$ (V vs Ag/Ag$^+$)	compd	$E_p{}^1$ (V vs Ag/Ag$^+$)
1a	1.07	**1h**	1.04
1b	1.02	**1i**	1.05
1c	1.04	**1j**	1.04
1d	0.89	**2a**	1.20
1e	0.82	**2b**	1.12
1f	0.75	**2c**	1.11
1g	0.98	[**7**	0.76][b]

[a] Experimental conditions: platinum bead anode; reference electrode, Ag/0.1 M $AgNO_3$ in MeCN; substrate, 3–8 mM in 0.1 M $LiClO_4$/MeCN; sweep rate 50 mV/s. [b] Refers to the tris(4-bromophenyl)amine mediator.

in its active form at the electrode (Scheme II).

Effective mediators must fulfill several conditions including chemical stability in both reduced and oxidized forms and also no redox reactions with other than the targetted compound must occur. In mediated electrolysis electron-transfer reactions can often be carried out using redox catalysts whose redox potentials are up to 600 mV lower than the corresponding potentials of the substrates. The observation of such catalysis depends upon the thermodynamically unfavorable reversible electron transfer to the substrate being followed by a fast and irreversible chemical reaction such as cleavage. Besides the advantage of lowering the potential at which reaction takes place, the number of transferred electrons in the first step can be controlled by a suitable choice of the redox catalyst. Several triarylamines are suitable as mediators, and tris(4-bromophenyl)amine (**7**) proved to be suitable for this work.

Voltammetric Experiments. In Table II is displayed the first oxidation peak potentials ($E_{pa}(1)$) for compounds **1a–j** and **2a–c**, determined by cyclic voltammetry at 50 mV s^{-1} [MeCN–0.1 M $LiClO_4$; Pt bead working electrode; Ag–0.1 M $AgNO_3$ in MeCN reference electrode; substrate concentrations ranging from 3 to 8 mM]. The oxidation waves were irreversible, and for several dimers a considerable decrease of current was observed on the second cycle; this is consistent with electrode fouling by polymerization. For compounds which have a free phenolic group at the 4-position, i.e. **1d–f**, the oxidation peaks are about 150 mV more negative than for the corresponding 4-methoxylated compounds. When the hydroxyl at C_α is replaced by a carbonyl, as in **2a–c**, the compounds are more difficult to oxidize and the peak potentials are shifted positively by ca. 100 mV. The first oxidation peak potential for the mediator **7**, under the same conditions, was +0.76 V, which is ca. 240 mV lower than for **1a–c,g–j** and ca. 350 mV than for **2a–c**. The 4-hydroxyl compounds **1d–f** are the most easily oxidized; the oxidation potential of **7** is coincident with that of **1f** and is 130 and 60 mV lower than those of **1d** and **1e**, respectively.

Several cyclic voltammetric experiments[11] were carried out to determine whether the radical cation generated anodically from amine **7** was involved in an irreversible oxidation of model dimers. A typical experiment is outlined in Figure 2. Curve a shows the voltammogram of amine **7** (0.8 mM) recorded at 50 mV s^{-1}. After addition of **1b** (8 mM, $E_{pa}(1)$, +1.02 V) the voltammogram was unchanged (Figure 2b). Addition of base 2,6-lutidine (16 mM), brought about an increase in the anodic peak current (i_{pa}) with a concomitant decrease in the cathodic peak current (i_{pc}) of the mediator (Figure 2c). This effect became more pronounced as the concentration of 2,6-lutidine was progressively increased, and at 190 mM in base the reduction peak was almost completely absent. At this lutidine concentration an increase in sweep rate to 200 mV s^{-1} caused a substantial restoration of the reduction current for the radical cation of **7** (Figure 2d). This is characteristic of a system where the rate of the irreversible follow-up chemical reaction involving the radical cation intermediate $[\mathbf{1b}]^{\bullet+}$, generated by oxidation with $[\mathbf{7}]^{\bullet+}$ is sufficiently slow as to allow interception of $[\mathbf{7}]^{\bullet+}$ in the reverse sweep. As the presence of base was essential for the electrocatalytic reaction it seems reasonable to assume that deprotonation of $[\mathbf{1b}]^{\bullet+}$ is the rate-determining step of the chemical follow-up reaction. The magnitude of the catalytic effect,[11] as determined by cyclic voltammetry for some of the substrates with $E_{pa}(1)$ in the 1.0-V region, indicated that preparative-scale indirect electrochemical oxidations would be possible albeit at rather slow rates. With compounds **2a–c** no electrocatalytic effect was observed; with **1d–f** indirect oxidation was not feasible as their oxidation potentials were similar to, or lower, than that of the mediator **7**.

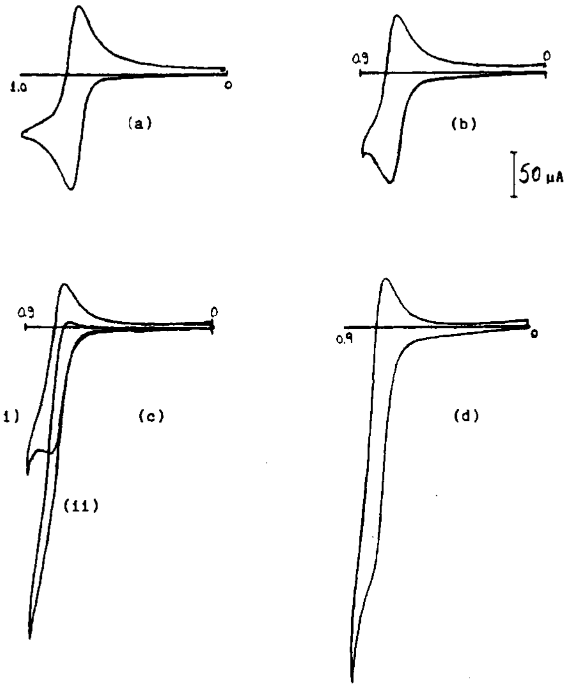

Figure 2. Cyclic voltammetry: MeCN–$LiClO_4$ (0.1 M); Ag/Ag$^+$ ref; (a) mediator (**7**, 0.8 mM), 50 mV s^{-1}; (b) (**7**, 0.8 mM and **1b**, 8 mM), 50 mV s^{-1}; (c) As for (b) with 2,6-lutidine [(i) 16 mM, (ii) 190 mM]; (d) as for (c, ii) at 200 mV s^{-1}.

Preparative Experiments. Key lignin model compounds were oxidized using tris(4-bromophenyl)amine (**7**) radical cation which was anodically regenerated at +0.76 V vs Ag/Ag$^+$ in MeCN–CH_2Cl_2 (4:1 v/v) containing $LiClO_4$ (0.2 M) and 2,6-lutidine (0.06–0.07 M). The ratio of lignin model compounds:mediator was usually 5:1, and the mediator was almost quantitatively recovered after the electrochemical experiments. The results of these experiments are summarized in Table III.

In these experiments the cleavage products for all substrates except **2b** were aldehydes; no guaiacol (**5**) was observed. In the case of **2b** the starting material was recovered unchanged. This is not surprising in view of the difficulty of oxidation of **2b** vis â vis **7** (Table II). In the other instances conversion is especially selective for compounds **1c–j** (Table III, entries 3–7) although a low current

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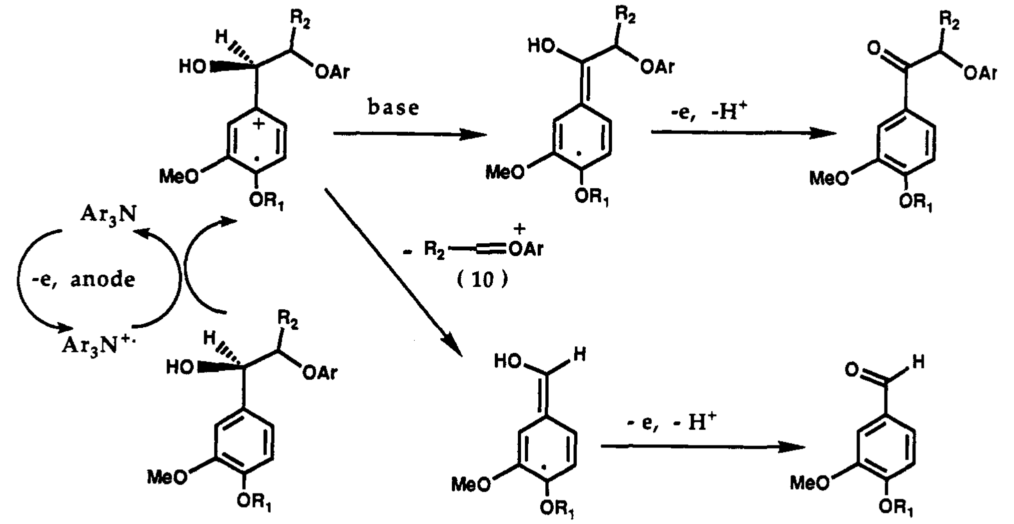
(11) Brinkhaus, K. H. G.; Steckhan, E.; Schmidt, W. *Acta Chem. Scand.* **1983**, *B37*, 499.

Table III. Mediated Electrochemical Oxidation of Lignin Model Dimers

entry	compd	method[a]/charge (F mol^{-1})	products (%)[b] aldehyde (3)	recovd starting material (%)	material balance (%)	efficiency (% for 2 F mol^{-1})
1	**1a**	A/4.0	20 (**3b**)	46	66[c]	27
2	**1b**	A/2.5	25 (**3c**)	50	75[d]	40
3	**1c**	A/0.6	5 (**3b**)	93	98	23.4
4	**1g**	AorB/1.7	10 (**3b**)	90	100	11.8
5	**1h**	AorB/1.5	10 (**3b**)	85	95	20
6	**1i**	B/3.6	25 (**3c**)	65	90[e]	19.4
7	**1j**	B/2.9	15 (**3e**)	83	98	11.8
8	**2b**	A/1.6	–	100	100	0

[a] Electrolysis procedures. Method A: divided cell, glassy carbon anode (4 cm^2); platinum cathode (1.5 cm^2); reference electrode, Ag/0.1 M $AgNO_3$ in MeCN; anolyte, 0.2 M $LiClO_4$ in $MeCN/CH_2Cl_2$ (4:1) (30 cm^3) containing 2,6-lutidine (66.7 mM), Na_2CO_3 (500 mg), tris(4-bromophenyl)amine (3.3 mM) and substrate (16.7 mM); catholyte, 0.2 M $LiClO_4$ in MeCN. Method B: undivided cell, electrodes see A; solution, 0.2 M LiClO *in* $MeCN/CH_2Cl_2$ (4:1) (50 cm^3) containing water (1% v/v), 2,6-lutidine (74 mM), Na_2CO_3 (500 mg), tris(4-bromophenyl)amine (3.4 mM), and the substrate (17 mM). Working potential in both methods +0.76 V. [b] Analyzed by standardized HPLC and calculated based on starting material. [c] Ketone **2a** (10%);[b] addition products derived from reaction at aromatic ring determined by ^1H NMR (ca. 15% of reaction mixture.). [d] Ketone **2b** (5%);[b] addition products derived from reaction at aromatic ring determined by ^1H NMR (ca. 10% of reaction mixture). [e] Ketone from OH oxidation of **1i** (5%).[b]

Scheme III



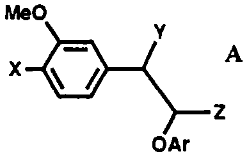
efficiency was observed in all cases. Compounds **1a**, **1b**, and **1i** afforded, besides the aldehydes formed by C_α–C_β bond cleavage, the corresponding ketones (Table III, entries 1, 2, and 7). Products from addition to the aromatic rings were also detected among the products from mediated oxidation of **1a** and **1b**. Ketone formation is in competition with C_α–C_β cleavage, and the outcome may well depend on the substitution pattern of the side chain. When 1-(3,4-dimethoxyphenyl)ethanol (**8**) was electrolyzed, under the same experimental conditions (1.8 F mol^{-1}), 3,4-dimethoxyacetophenone (**9**) (65%) was the only product besides recovered **8** (35%); the current efficiency was 72% based on a 2e process. No cleavage product was observed.

Mechanistic Rationalization. Oxidative cleavage at nickel requires relatively high temperatures and alkaline solution. The structural requirements for oxidative cleavage of the C_α–C_β bond are summarized, qualitatively, in Table IV, which draws upon the detailed results given in Tables I and III. The key results which must be reconciled in a mechanistic rationalization are as follows.

(a) In all cases the β-*O*-aryl ether function is essential for cleavage. (b) For oxidative cleavage at a nickel anode, in alkaline solution, the compound must contain either a 4-hydroxyl group, or a β-CH_2OH group, or a carbonyl at C_α. (c) Chemical reaction in alkali at high temperature, prior to electrolysis, is very important; the most significant of such reactions requires the presence of a 4-hydroxyl function. Under these conditions enol ethers such as **6** are formed. These appear to be intermediates, not for cleavage, but probably for competing polymerization. (d) Mediated electrolysis, which is initiated unequivocally by single one-electron homogeneous oxidation, gives selective cleavage and does not depend upon the structural conditions listed above. The relative oxidation potentials of mediators and substrate are all-important; for compound **2b** mediated oxidative cleavage does not take place probably because its oxidation potential is too high. (e) The presence of a base, such as 2,6-lutidine, is necessary for successful mediated oxidative cleavage. (f) Where CH_3 is the C_β function (compound **8**), mediated oxidation gives the C_α ketone with no C_α–C_β cleavage.

Mediated Electrolysis. The requirement that the substrate oxidation potentials are close to that of the mediator (Table II) and the observation of formation mainly of aldehyde product points to the relatively straightforward mechanism outlined in Scheme III. The reaction is initiated by homogeneous single-electron transfer. After cleavage of the C_α–C_β bond, further electron transfer is required to produce the aldehyde and addition of a base is required for the essential and probably slow deprotonation. The observation of α-ketonic products (Table III, entries 1, 2, and 6) is explained in terms of deprotonation at C_α competing with cleavage of the C_α–C_β bond. In the absence of a β-*O*-aryl function oxidation to carbonyl is the only reaction; the conversion of **8** into **9** has been described above. The driving force for the predominant reaction when a β-*O*-aryl function is present (C_α–C_β

Table IV. Qualitative Requirements for C_α–C_β Cleavage



Ar = 2-methoxyphenyl

			cleavage by:	
X	Y	Z	Ni anode/ alkali	mediator/ MeCN
MeO	HO	H	no	yes
MeO	HO	Me	no	yes
MeO	HO	CH_2OH	yes	yes
MeO	=O	H	yes	–[a]
$PhCH_2O$	=O	H	–	no[a,b]
MeO	=O	Me	yes	–[a]
HO	HO	H	yes	–[c]
HO	HO	CH_2OH	yes	–[c]
MeO	HO	CO_2Et	–	yes

[a] No interaction substrate–mediator by cyclic voltammetry. [b] Oxidation potential of substrate too high for mediated electrolysis with tris(4-bromophenyl)amine. [c] Oxidation potential close to that of mediator.

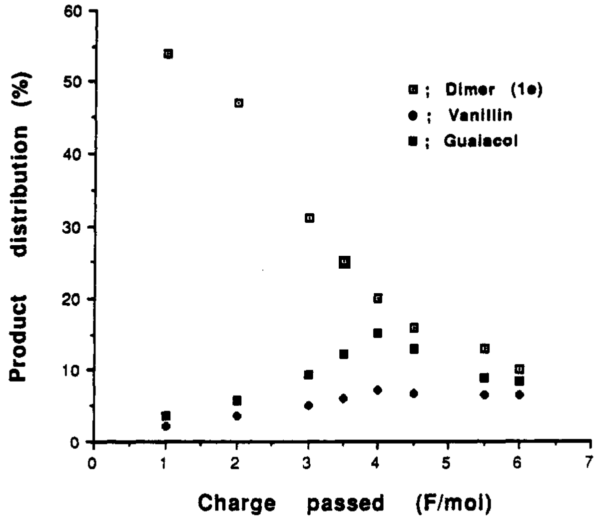


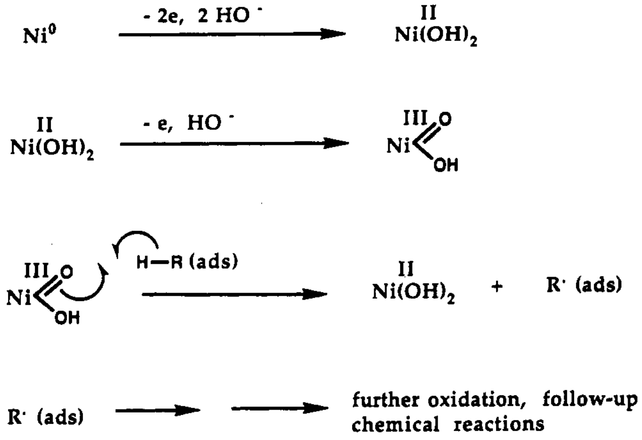
Figure 3. Reaction profile for electrolysis of dimer **1e** [electrolyte 2 M aqueous NaOH, at 150 °C, pretreatment for 1 h prior to electrolysis at a Ni anode; product analysis by HPLC].

cleavage) is formation of the stabilized oxonium cation (**10**).

Electrolysis at a Nickel Anode. The electrooxidative cleavage at nickel of various lignins has been reported.[4a] The optimum conditions for formation of low molecular weight products such as vanillin are those associated with formation of a Ni(III), oxygenated, anode surface.[12] In particular the electrolyte is 2–3 M aqueous sodium hydroxide, and relatively low nominal current densities are employed (<1 mA cm^{-2}). Under such conditions alcohols are usually oxidized to carboxylic acids;[12] it is unlikely that aldehydes are formed en route because separate conversion, at nickel anodes, of aromatic aldehydes into carboxylic acids requires significantly different conditions.[12]

At the nickel anode one of the lignin model dimers (**1e**) was shown smoothly to be consumed. The low molecular products (vanillin, guaiacol) were clearly formed by electrolysis (Figure 3), although much polymerization occurred. There are several structural features which distinguish the lignin model dimers from simple benzylic alcohols and which are crucial for oxidative cleavage. These have been listed above but essentially are the 4-hydroxyl group, the β-*O*-aryl group, and the β-CH_2OH function. In addition, efficient cleavage is seen for the α-ketonic derivatives. It is widely accepted[12] that the Ni(III) anode effectively abstracts hydrogen atoms in initiating oxidation. The sequence of reactions is conveniently represented in Scheme IV.

Scheme IV



For phenols complex reactions are observed[12] except for 2,6-di-*tert*-butylphenol, which is smoothly dimerized into the corresponding diphenoquinone. A hydrogen abstraction route is unlikely for this compound so single-electron oxidation of the phenoxide ion is implicated.

The reactions important for nickel anode conversion of the lignin model dimers will therefore include both hydrogen abstraction and single-electron oxidation (SET). Although unusual for the alkaline nickel anode, SET might occur via a mediator, e.g. oxidized phenoxide species. Ketones are likely to be formed by hydrogen abstraction, and these are known further to oxidize to the acids (Table I, entries 7 and 8). The important role of the β-CH_2OH group may be to template the system to assist hydrogen abstraction from the benzylic α-position via e.g. **11** in Scheme V. The 4-hydroxyl compounds (phenols) will be completely ionized in the alkaline medium and consequently easily oxidized by single-electron transfer. Thus the 4-hydroxyl compounds give significant amounts of aldehyde (Table I, entries 3–5) and no acid; this behavior is analogous to that observed for mediated electrolysis which is unambiguously via single-electron transfer (SET). In contrast, the 4-methoxyl compound **1g** gives both acid and aldehyde (Table I, entry 6), which probably indicates initiation by either SET or hydrogen abstraction; the latter would proceed via the ketone and is the more important pathway. These suggested routes are summarized in the reactions given in Scheme V, which also includes the suggested route for chemical conversion into the enol ethers, e.g. **6**.

The postulation of the intermediate **11** requires further discussion. It has been shown herein that the presence of the β-CH_2OH group greatly facilitates cleavage. This is consistent with reports[12] that simple diols are oxidized, according to cyclic voltammetric experiments, faster than the corresponding monohydric alcohols. These observations are accommodated in the suggested intermediacy of a templated structure of the type **11**. From all that is presently known about anodic oxidation at nickel anodes in alkali such an intermediate would be a surface species.

Experimental Section

General. ^1H and ^{13}C spectra were recorded on either a Bruker 250- or a 400-MHz instrument, and chemical shifts, in ppm, are

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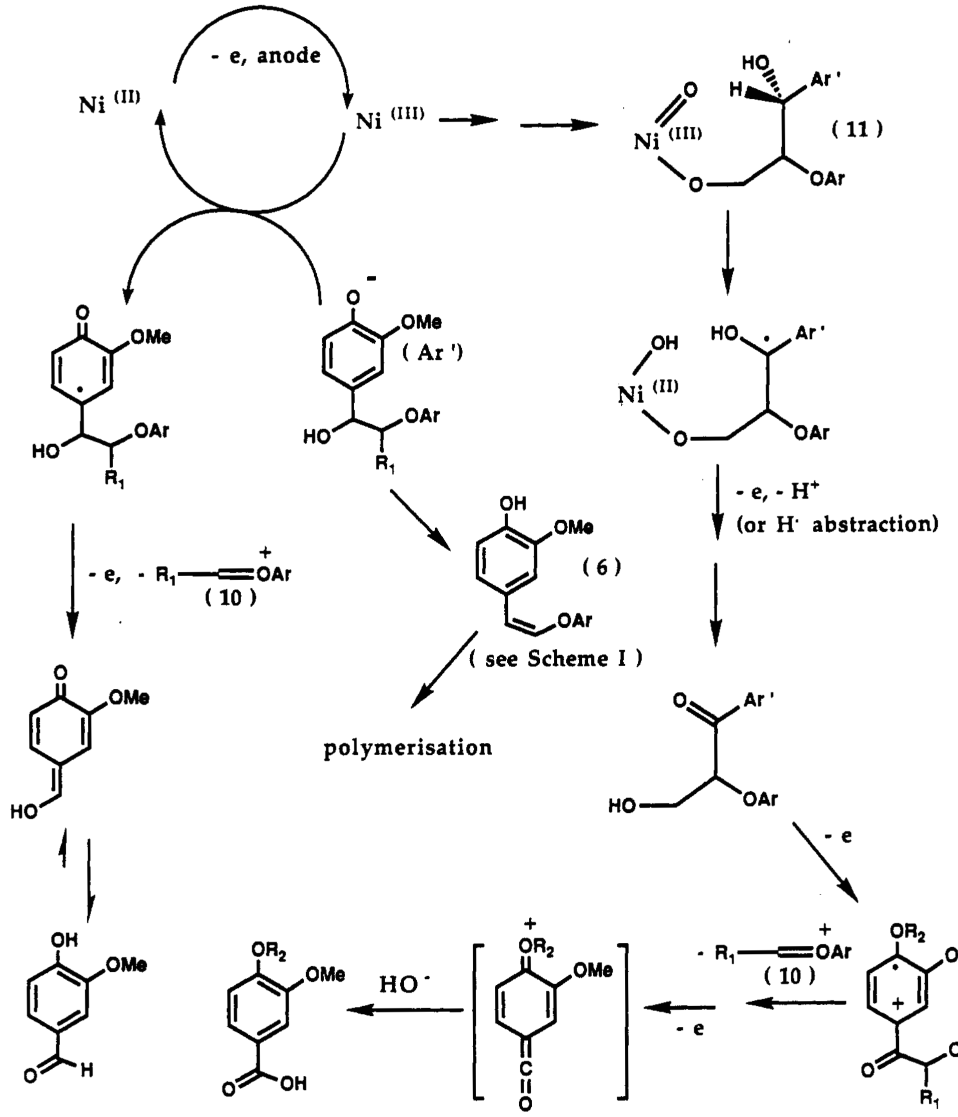
[12] Schäfer, H. J. *Top. Curr. Chem.* **1987**, *142*, 101.

Scheme V



i.e. aldehyde by direct SET, acid formation initiated by surface reaction

referred either to TMS or to acetone-d_6. Mass spectra were obtained on a Kratos MS50 double-focusing spectrometer in the electron impact (EI) mode. Peaks reported here were either considered structurally significant or had an intensity greater than 2% of the base peak. The mixtures of phenolic compounds were analyzed by gradient elution HPLC with UV detection of eluants at 289 nm. A C18 (Chromapack), reverse-phase column 25 cm × 4.6 mm i.d. was employed with a 5-μL sample injection and programmed elution (methanol/1% acetic acid in water) at 1.0 mL min^{-1} at room temperature. The HPLC detector was calibrated with mixtures of authentic samples of known composition. IR spectra, mostly as KBr disk samples, were recorded on a Perkin-Elmer 1600 FTIR spectrometer. All materials were purchased from Aldrich Chemical Co. or BDH and used as received unless indicated otherwise. THF was distilled from sodium/benzophenone under dry nitrogen.

Cyclic voltammetric experiments were run in an undivided cell using a platinum bead working electrode. The reference electrode was Ag/AgNO$_3$ (0.1 M in acetonitrile) and the counter electrode was a platinum coil. The electrolyte was 0.1 M LiClO$_4$ in acetonitrile, and the concentration of the substrates was 3–8 mM.

General Procedure for Direct Electrolysis. (a) Room Temperature. For these electrolyses an undivided cell was used made of glass and equipped with a nickel foil anode (6.25 cm^2) and nickel cathode (1 cm^2). The dimers **1a**, **1d**, and **1** (14–16 mM) were electrolyzed in 1.0 M aqueous NaOH/*t*-BuOH (1:1 v/v) (20 cm^3) at constant current (30 mA). After passage of 6–15 F mol^{-1} the mixture was neutralized with acetic acid, diluted with methanol to 50 cm^3, and analyzed by HPLC.

(b) High Temperature. The cell was constructed of stainless steel and equipped with a PTFE liner (40 cm^3 volume); the top was also lined with PTFE and fitted with O-ring rubber seals and a safety valve (80 psi). The anode was a nickel gauze cylinder (30 cm^2, 40 mesh), and this was surrounded by a pair of concentric stainless steel cylinders as cathode. The dimers **1a**, **1c**, **2a**, and **2c** (14–16 mM) were electrolyzed in 1.5 M aqueous NaOH/*t*-BuOH (1:1 v/v) (20 cm^3) at constant current, 50 mA. The autoclave cell was heated in a silicone oil bath (150–160 °C) for 1 h before and then throughout the passage of the charge (6 F mol^{-1}). For the compounds **1d**, **1e**, **1f**, and **1g** an alkaline aqueous solution (2.0 M NaOH, 20 cm^3) was the solvent. After completion the mixture was neutralized with acetic acid, diluted with methanol to 50 cm^3, and analyzed by HPLC.

General Procedure for Indirect Electrolysis. (a) Divided Cell. The tris(4-bromphenyl)amine (**7**, 0.1 mmol) dissolved in 30 cm^3 CH$_3$CN/CH$_2$Cl$_2$ (4:1 v/v) (0.2 M LiClO$_4$) together with 2,6-lutidine (2.0 mmol) and Na$_2$CO$_3$ (4.7 mmol) was transferred to the anode chamber of a divided H-type glass cell. The cathode chamber was filled with 15 cm^3 CH$_3$CN/0.1 M LiClO$_4$. The electrodes used were a glassy carbon (4 cm^2) with a platinum cathode and a Ag/AgNO$_3$ (0.2 M in CH$_3$CN) reference electrode. Preelectrolysis at the mediator oxidation potential (+0.76 V) was performed until a very intense blue color appeared (typical for triarylamine radical cations). Subsequent addition of the substrates (0.5 mmol) resulted in the disappearance of the color. Electrolysis was continued until the current dropped to about 3 mA. After adding water, the mixture was extracted with CH_2Cl_2 (3 × 20 cm^3), washed with water (3 × 10 cm^3), and dried over $MgSO_4$. Yields were determined by HPLC.

(b) Undivided Cell. The tris(4-bromophenyl)amine (**7**, 0.17 mmol) dissolved in 50 cm^3 CH_3CN/CH_2Cl_2 (4:1 v/v) (0.2 M $LiClO_4$) together with 2,6-lutidine (3.7 mmol) and 1% v/v of water was transferred to an undivided beaker type glass cell which was equipped with a glassy carbon anode (4 cm^2), Ag/$AgNO_3$ (0.2 M CH_3CN) reference electrode, and Pt cathode (1.5 cm^2). After electrolysis at +0.76 V the typical intense blue color appeared, and upon addition of 0.83 mmol of the substrate the current doubled. The electrolysis mixture was worked up as described above.

Synthetic Procedure for Compounds 1a–c and 3a–c. (a) Bromination of Acetophenone Derivatives. To a stirred solution of the appropriate acetophenone (83.2 mmol) in chloroform (50 cm^3) was added quickly a solution of bromine (13.3 g, 83.2 mmol) in chloroform (20 cm^3). The evolution of HBr was vigorous. After refluxing the solution for 20 min, the solvent was removed under reduced pressure, affording a crystalline mass. Recrystallization from methanol gave the brominated derivatives as follows. 2-Bromo-1-(3,4-dimethoxyphenyl)-1-ethanone, mp 80–1 °C (lit.[13] mp 80–1 °C), 45.4% yield; 2-bromo-1-(3,4-dimethoxyphenyl) 1-propanone, mp 82–3 °C (lit.[13] mp 81–2 °C), 85.0% yield; 2-bromo-1-[4-(phenylmethoxy)-3-methoxyphenyl]-1-ethanone, mp 102–3 °C (lit.[14] mp 93–102 °C), 72% yield.

(b) Replacement with Guaiacol (2a–c). To a stirred solution of guaiacol (1.35 g, 10.9 mmol) in acetone (20 cm^3) were added the appropriate bromine derivative (10.7 mmol) and K_2CO_3 (1.53 g, 11 mmol). The inorganic salts were filtered off and washed with acetone. The combined filtrates were concentrated under reduced pressure. The residue was dissolved with dichloromethane, and the solution was washed successively with water and brine, dried over $MgSO_4$, and stripped in vacuo to give a single, crystalline compound.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanone (2a): mp 95–6 °C (methanol) (lit.[15] mp 93.5–94.5 (ethanol)); 97% yield.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone (2c): mp 117–120 °C (methanol).[16]

(c) Reduction with $NaBH_4$ (1a–c). To a stirred solution of $NaBH_4$ (0.33 g, 8.7 mmol) in methanol (3.5 cm^3) was added quickly a solution of ketones **2a–c** (3.0 mmol) in methanol 938 cm^3). After 30 min acetic acid (10 cm^3) was added in water (67 cm^3) and shaken with CH_2Cl_2 (4 × 50 mL). The organic layer was washed successively with water and sodium bicarbonate solution, dried over $MgSO_4$, and concentrated in vacuo to give a single, crystalline compound.

3,4-Dimethoxy-*α*-[(2-methoxyphenoxy)methyl]benzenemethanol (1a): mp 128–9 °C (methanol) (lit.[15] 129.5–131 °C (ethanol)); 98% yield.

3-Methoxy-*α*-[(2-methoxyphenoxy)methyl]-4-(phenylmethoxy)benzenemethanol (1b): mp 71–72 °C (methanol); 90% yield.

3,4-Dimethoxy-*α*-[1-(2-methoxyphenoxy)ethyl]benzenemethanol (1c): syrup mixture of erythro and threo (33:1),[8b] 97% yield.

Synthetic Procedure for Compounds 1e–g. Aldol Condensation (1h–j). Ethyl (2-methoxyphenoxy)acetate was synthesized according to the method of Nakatsubo et al.:[17] bp 100 °C (0.15 mmHg); 76% yield. To a stirred solution containing 1.12 cm^3 (8.0 mmol) of diisopropylamine freshly distilled from sodium metal in 20 cm^3 of anhydrous THF was added 5.55 cm^3 *n*-butyllithium solution (1.6 M) at 0 °C over a period of 15 min, under nitrogen and stirring during and after the addition (30 min). After the reaction mixture was cooled to −75 °C, ethyl (2-methoxyphenoxy)acetate (1.55 g, 7.4 mmol) dissolved in 25 cm^3 of THF was added dropwise over a period of 1 h, followed by addition of the appropriate benzaldehyde derivative (**3b**, **3c**, and **3e**) dissolved in THF (25 cm^3). After stirring for an additional 90 min at −75 °C, the reaction mixture was neutralized with powdered dry ice and partitioned between ethyl acetate and water. The ethyl acetate solution was dried over $MgSO_4$ and concentrated under reduced pressure to give 1-(3,4-dimethoxyphenyl)-2-carbethoxy-2-(2-methoxyphenoxy)ethanol (**1b**): mp (erythro) 87–91 °C (ethyl acetate/*n*-hexane); 95% yield; MS (relative intensity) 377 (2), 376 (10), 358 (3), 236 (3), 211 (6), 180 (2), 168 (3), 166 (9), 165 (9), 164 (2), 151 (4), 139 (13), 138 (9), 137 (100), 135 (3), 123 (5), 122 (3), 121 (4), 109 (7), 108 (5); M$^+$ = 376.1523; ^{1}H NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 1.12 (t, *J* = 14 Hz, 3 H), 3.78 (s, 6 H), 3.81 (s, 3 H), 4.11 (q, *J* = 14 Hz, 2 H), 4.70 9d, *J* = 16 Hz, 1 H), 5.03 (d, *J* = 16 Hz, 1 H), 6.7–7.02 (m, 6 H), 7.20 (d, *J* = 2 Hz, 1 H); ^{13}C NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 12.4, 54.1, 54.2, 54.5, 59.7, 72.4, 81.5, 110.1, 111.9, 114.7, 118.5, 119.7, 121.6, 132.5, 146.2, 147.7, 148.9, 168.8; IR (KBr) 3484, 1733, 1517, 1496, 1254, 1028 cm^{-1}. Ethyl *β*-hydroxy-3-methoxy-*α*-(2-methoxyphenoxy)-4-(phenylmethoxy)benzenepropanoate (**1i**): mp (erythro) 80–81 °C (ethyl acetate/hexane) [lit.[17] mp 80.5–81 °C (ethanol/hexane)]; 90% yield. 1-[3,5-dimethoxyphenyl-4-(phenylmethoxy)phenyl]-2-carbethoxy-2-(2-methoxyphenoxy)ethanol (**1j**).

Crystallization from ethyl acetate gave 1.2 g of the erythro diastereoisomer. The filtrate was evaporated, and the residue was chromatographed on a SiO_2 column (Merck 60) (ethyl acetate/petroleum ether (35–60 °C/1:3). A mixture of erythro/threo (1.1 g) and pure threo (0.2 g) were obtained, overall yield 71%: mp (erythro) 117–119 °C (ethyl acetate); MS (relative intensity) *m/e* 483 (2), 482 (8), 373 (2), 273 (14), 272 (5), 239 (3), 221 (5), 211 (3), 209 (2), 181 (4), 137 (31), 135 (2), 125 (3), 123 (5), 122 (6), 121 (4), 109 (10), 108 (3), 93 (3), 92 (8), 91 (100), 81 (4), 78 (2), 77 (11), 65 (10), 64 (2), 59 (46); M$^+$ 482.1932; ^{1}H NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 1.16 (t, *J* = 7 Hz, 3 H), 3.78 (s, 3 H), 3.81 (s, 6 H), 4.14 (q, *J* = 7 Hz, 2 H), 4.69 (d, *J* = 6.5 Hz, 1 H), 4.91 (s, 2 H), 5.06 (d, *J* = 6.5 Hz, 1 H), 6.71–6.99 (m, 6 H), 7.25–7.48 (m, 5 H); ^{13}C NMR ($(CD_3)_2CO/D_2O$ 9:1) 12.5, 54.5, 59.7, 72.6, 73.2, 81.2, 103.4, 111.7, 114.3, 119.7, 121.5, 137.2, 148.1, 152.0, 168.3; IR (KBr) 3526, 1739, 1594, 1506, 1457, 1421, 1327, 1264, 1253, 1221, 1181, 1151, 1126, 1069, 1049, 1022, 739 cm^{-1}; mp (threo) 119–123 °C; MS (relative intensity) *m/e* 482 (5), 374 (2), 273 (10), 272 (6), 252 (2), 221 (4), 211 (2), 181 (3), 138 (2), 137 (22), 135 (2), 123 (5), 122 (4), 121 (3), 109 (12), 92 (8), 91 (100), 81 (6), 78 (10), 70 (2), 65 (9), 59 (32), 45 (5); M$^+$ 482.1945; ^{1}H NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 1.06 (t, *J* = 7 Hz, 3 H), 3.79 (s, 3 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 4.03 (q, *J* = 7 Hz, 2 H), 4.80 (d, *J* = 5.5 Hz, 1 H), 4.90 (s, 2 H), 5.09 (d, *J* = 5.5 Hz, 1 H), 6.67–6.99 (m, 6 H), 7.24–7.50 (m, 5 H); ^{13}C NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 12.4, 54.4, 54.5, 59.8, 73.2, 73.3, 81.5, 102.7, 103.3, 111.7, 113.7, 119.8, 121.2, 137.2, 148.3, 152.1, 152.3, 168.3; IR (KBr) 3467, 1756, 1594, 1505, 1460, 1420, 1330, 1251, 1226, 1183, 1126, 1076 cm^{-1}.

Reduction with $LiAlH_4$ and Catalytic Hydrogenolysis. To a stirred solution containing $LiAlH_4$ (0.54 g, 14.2 mmol) in anhydrous THF (20 cm^3) were added dropwise the appropriate erythro or erythro-rich carbethoxy compounds (**1h–j**) dissolved in 30 cm^3 of THF over a period of 30 min at 55 °C. Stirring was continued for an additional 3 h. The reaction mixture was cooled to 0 °C, and a solution of water (3 cm^3) in THF (16 cm^3) was dropped into the mixture to decompose excess $LiAlH_4$. The lithium complex was decomposed by addition of aqueous hydrochloric acid, and products were extracted with CH_2Cl_2 (3 × 20 cm^3). The organic phase was dried ($MgSO_4$), and the solvent was evaporated in vacuo to give a single, colorless compound. This was dissolved in 50 cm^3 of ethanol containing 0.36 g of 10% Pd/C and stirred under hydrogen (20 psi) for 2 h. The solvent was evaporated under reduced pressure.

***erythro*-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1g)**: syrup; 90% yield (lit.[18]).

***erythro*-1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1e)**: syrup; 91% yield (lit.[17]).

***erythro*-1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1f)**: syrup; 72% yield (lit.[19]

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threo); MS (relative intensity) m/e 196 (2), 150 (100), 140 (3), 137 (2), 123 (12), 121 (5), 109 (10), 93 (2), 91 (2), 77 (7), 65 (4); M^+ 352.1427; ^1H NMR (($(CD_3)_2CO/D_2O$, 9:1) δ 3.76 (s, 6 H), 3.80 (s, 3 H), 3.90 (dd, $J = 5$ Hz, $J = 11$ Hz, 2 H), 4.40 (m, 1 H), 4.92 (d, $J = 5$ H, 1 H), 6.78–7.00 (m, 6 H); ^{13}C NMR (($(CD_3)_2CO/D_2O$, 9:1) δ 56.3, 56.4, 61.8, 73.9, 85.6, 105.5, 113.6, 118.4, 122.1, 123.1, 133.3, 148.5, 148.9, 151.5.

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Registry No. **1a**, 17078-88-5; **1b**, 67015-29-6; **1c**, 1835-10-5; **1d**, 20679-57-6; **1e**, 7382-59-4; **1f**, 136863-16-6; **1g**, 10535-17-8; **1h**, 7572-96-5; **1i**, 58497-34-0; **1i** ketone, 7572-91-0; **1j**, 136863-17-7; **2a**, 22675-96-3; **2b**, 22317-29-9; **2c**, 1835-09-2; **3a**, 121-33-5; **3b**, 120-14-9; **3c**, 2426-87-1; **3d**, 134-96-3; **3e**, 6527-32-8; **4a**, 93-07-2; **4b**, 121-34-6; **5**, 90-05-1; lignin, 9005-53-2.

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The Triplex Diels–Alder Reaction: Intramolecular Cycloaddition of Phenyl-Substituted Alkenes to 1,3-Dienes

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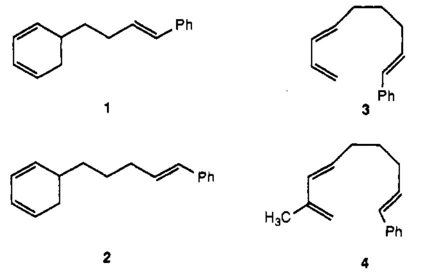
The triplex Diels–Alder reaction of dienes and styrene-like dienophiles that are covalently linked with a flexible alkyl chain was investigated. Sensitization with 9,10-dicyanoanthracene in benzene solution leads to good yields of [4 + 2] adducts when the diene is a derivative of cyclohexadiene and the linking chain contains two atoms. If the linking chain contains three atoms, dyotropic transfer of hydrogens occurs. When acyclic dienes are employed, it is believed that conformational isomers lead to mixtures containing considerable yields of both [4 + 2] and [2 + 2] cycloadducts.

Introduction

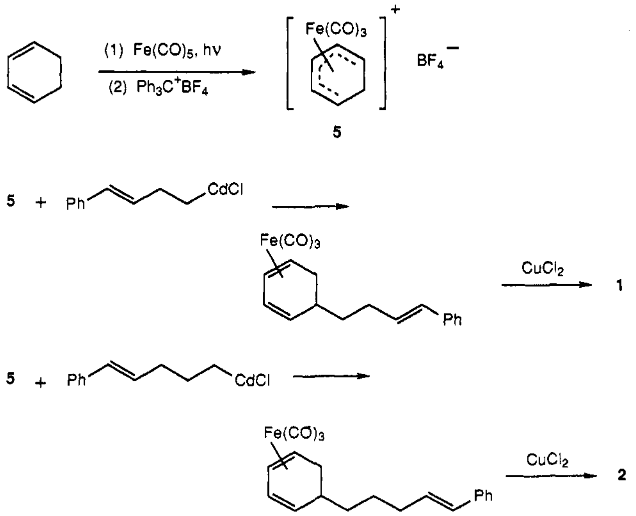
The triplex Diels–Alder reaction provides a useful photochemical adjutant to the conventional thermal, Lewis acid-catalyzed, and radical cation modalities of this cycloaddition reaction when both the diene and dienophile are electron-rich.[1] In recent reports we described the application of this approach to the stereospecific cycloaddition of methylstyrenes to 1,3-cyclohexadiene[2] and its expansion to the intermolecular addition of 1,3-dienes to enolic, alkenyl, and acetylenic dienophiles.[3] Additional interest in this reaction has been sparked by the discovery that irradiation of the optically active, electron-deficient catalyst (−)-1,1′-bis(2,4-dicyanonaphthalene) gives the endo-trans-[4 + 2] cycloadduct of *trans*-β-methylstyrene and 1,3-cyclohexadiene in 15% enantiomeric excess.[4]

There are significant limitations to application of the triplex Diels–Alder reaction. Two of these are competing dimerization of the diene when its concentration is high and troublesome [2 + 2] cycloaddition of the diene to the dienophile. We sought to overcome these problems by covalently linking the diene and the dienophile. In this intramolecular version, we hoped that the local concentration of diene would be high enough to intercept a short-lived exciplex of sensitizer and dienophile without production of diene dimers. Similarly, it was postulated that conformational and ring strain related restriction associated with the linking group might require exclusive operation of the [4 + 2] cycloaddition mode. These hypotheses were tested by examination of the intramolecular triplex Diels–Alder reaction of phenyl-substituted alkenes linked to acyclic 1,3-dienes and to a linked cyclohexadiene. The results of this investigation reveal certain advantages and restrictions of the intramolecular triplex reaction.

Chart I. 1,3-Dienes Linked to *trans*-Styrene Dienophiles



Scheme I. Syntheses of Compounds 1 and 2



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