Table I. Cyclic Voltammetric Data for 4 and Some Related Compounds

	$E_2{}^{ox}$	$E_1{}^{ox}$	$E_1{}^{red}$	$E_2{}^{red}$	$E_1{}^{sum}$ e	$E_2{}^{sum}$ f
4^a	+0.83	+0.39	−1.12	−1.35	1.51	2.18
1^b	+1.04	+0.68	−2.12	−2.64	2.80	3.68
2^b	+1.08	+0.68	−2.02	−2.42	2.70	3.50
perylene^c	+1.59	+1.06	−1.66	−2.19	2.72	3.78
TCVDMA^d		+0.96	−0.70		1.66	

^{a} This work, measured vs. SCE in DMF (8.0×10^{-4} M) with 0.1 M Et$_4$NClO$_4$ as supporting electrolyte at −50 °C; sweep rate = 7 mV/s. ^{b} Reference 4. ^{c} Reference 7. ^{d} *p*-(Tricyanovinyl)-*N,N*-dimethylaniline, ref 16. ^{e} $E_1{}^{sum} = E_1{}^{ox} + (-E_1{}^{red})$. ^{f} $E_2{}^{sum} = E_2{}^{ox} + (-E_2{}^{red})$.

Scheme II
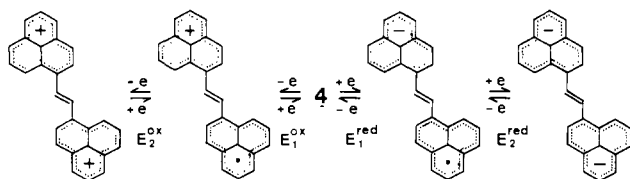
A reasonable key intermediate for the synthesis of **4** is the diphenalenylacetylene **9**, which might be converted to **4** by an appropriate isomerization procedure. The ethynyl alcohol **7a**, prepared in 97% yield by ethynylation of phenalanone (**6**) with lithium acetylide in THF at −78 °C, was converted to its methyl ether **7b** (NaH and then CH$_3$I in THF, 45–50 °C) in 93% yield as colorless oil. The lithium salt of **7b** (BuLi in THF, −78 °C) was treated with **6** to give the acetylene **8** in 46% yield as a pale yellow solid. Dehydration of **8** with a catalytic amount of β-naphthalenesulfonic acid in benzene at 80 °C for 10 min afforded **9** as an isomeric mixture. Isomerization of the mixture into the final compound **4**, as dark violet needles, mp 243–246 °C (dec),[14] was achieved by treatment with a large excess of triethylamine in dichloromethane (34% yield based on **8**).

The electrochemical behavior of **4** was studied by cyclic voltammetry, and the results are summarized in Table I together with the corresponding data reported for some related compounds. The sums of redox potentials, $E_1{}^{sum}$ and $E_2{}^{sum}$, are also listed in the Table I. The most striking feature is that the span of the second oxidation and reduction potentials of **4** ($E_2{}^{sum}$ = 2.18 V), not to mention that of the first potentials ($E_1{}^{sum}$ = 1.51 V), is substantially smaller than the $E_1{}^{sum}$ of the related hydrocarbons reported so far.[7,15] Furthermore, the $E_1{}^{sum}$ of **4** can be compared to that of the nonhydrocarbon molecule *p*-(tricyanovinyl)-*N,N*-dimethylaniline (TCVDMA), which comprises both the electron donor and acceptor moieties and exhibits the intermolecular π-amphoteric character in solid state.[16]

Such small values of E^{sum} observed for **4** can be attributed to the considerable electronic stability of the three oxidation states of the phenalenyl moiety, which are expected to be created in all of the redox states of **4** as shown in Scheme II.

Further studies are now in progress to design and synthesize novel conjugated hydrocarbons having small E^{sum} values in which intriguing chemical and physical properties might be expected.

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Registry No. 4, 50472-56-5; 6, 518-85-4; 7a, 80631-49-8; 7b, 80631-50-1; 7b lithium salt, 80631-51-2; 8, 80631-52-3; 9, 80631-53-4.

(13) All new compounds afforded proper combustion analyses as well as suitable IR and NMR spectra.

(14) **4**: UV/vis λ_{max} (in THF) 704 sh (log ϵ 2.94), 583 (5.17), 539 (4.79), 500 (4.30), 470 (3.74), 436 sh (3.15), 408 sh (3.11), 367 (3.46), 334 sh (3.83), 320 sh (3.98), 304 sh (4.22), 280 nm (4.11). The geometrical structure of **4** with C_{2h} symmetry as shown in the text was confirmed unambiguously through its 400-MHz ^{1}H NMR spectrum δ (CS$_2$ + CD$_3$COCD$_3$) 6.93 (d, J = 9.7 Hz, H$_3$), 7.20 (d, J = 7.3 Hz, H$_4$), 7.29 (dd, J = 8.3, 7.3 Hz, H$_5$), 7.45 (dd, J = 8.0, 8.0 Hz, H$_8$), 7.53 (d, J = 8.3 Hz, H$_6$), 7.58 (d, J = 9.7 Hz, H$_2$), 7.63 (d, J = 8.0 Hz, H$_7$), 7.91 (s, H$_{10}$), 8.22 (d, J = 8.0 Hz, H$_9$). Furthermore, small long-range coupling through five bonds between H^3 and H^{10} (also H$^{3'}$ and H$^{10'}$) (zigzag path) together with the substantial NOE (20%) between H^2 and H$^{10'}$ (also H$^{2'}$ and H^{10}) could be observed.

4
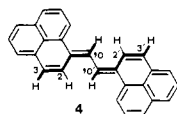
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Ruthenium-Catalyzed Oxygenation of Catechols to Muconic Acid Anhydrides and 2H-Pyran-2-ones. Intradiol and Extradiol Cleavage of the Carbon–Carbon Bond

Masakatsu Matsumoto* and Keiko Kuroda

Sagami Chemical Research Center Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

Pyrocatechase and metapyrocatechase are nonheme iron oxygenases capable of oxidatively opening catechol (**1**) by inserting both atoms of molecular oxygen into the substrate.[1] The former causes the intradiol ring cleavage, while the latter sets off the extradiol ring opening. Two types of mechanisms have been proposed for the pyrocatechase reaction: the first includes the formation of the dioxetane intermediate **2** (Hayaishi[2] and Grinstead[3]), and the second is a path through an anhydride **3**, which is more thermodynamically favorable than the dioxetane (Hamilton).[4] Although there have been several nonenzymatic approaches by the use of singlet oxygen,[5] superoxide ion,[6] and a combination of molecular oxygen and copper complexes[7] or iron complexes,[8] none of them have provided a direct evidence of the intermediates **2** or **3**.

1   2   3
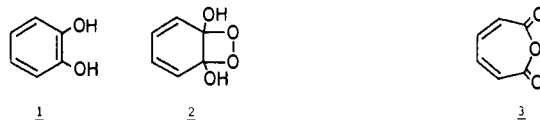
We report here a nonenzymatic oxygenation of catechols with molecular oxygen activated by ruthenium, which is just below iron

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(7) (a) Tsuji, J.; Takayanagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 7349. (b) *Tetrahedron Lett.* **1975**, 1245. (c) Rogić, M. M.; Demmin, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1976**, *98*, 7441. (d) Brown, D. G.; Beckmann, L.; Ashby, C. G.; Vogel, G. C.; Reimprecht, J. T. *Tetrahedron Lett.* **1977**, 1363. (e) Rogić, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472.

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in the periodic table. The characteristic features of the reaction are as follows: (i) the catechols are oxygenated into the Hamilton intermediates 3 (intradiol type) and 2*H*-pyran-2-ones (extradiol type, vide infra), (ii) the oxygenation proceeds through an *o*-quinone intermediate, and (iii) the atom of oxygen molecule is incorporated as the endocyclic oxygen of the products.

A solution of 3,5-di-*tert*-butylcatechol (4) (2 mmol) and RuCl₂(PPh₃)₃ (5) (0.7 mmol) in 1,1,2,2-tetrachloroethane (TCE) (15 mL) was stirred under an oxygen atmosphere (1 atm) at room temperature for 15 h (about 3 mmol of oxygen was consumed). The resulting dark blue solution was concentrated in vacuo, and the residue was chromatographed on silica gel. Elution with CH₂Cl₂ gave the muconic acid anhydride 6 (26% yield)[9] and the 2*H*-pyran-2-one 7 (64% yield).[10] This oxygenation is significantly different from the Baeyer–Villiger reaction of the quinone 8, which selectively affords the anhydride 6.[11]
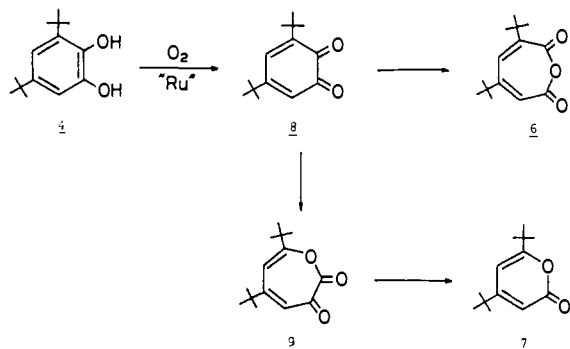
The GLC analysis following the time course of the oxygenation of 4 disclosed that (i) the quinone 8 was rapidly formed in the early stage of the reaction and then gradually disappeared, (ii) compound 9 in addition to 6, 7, and 8 appeared at the midway of the reaction, and (iii) after 4 and 8 disappeared, the pyrone 7 increased, while the compound 9 decreased. The compound 9 was assigned to a seven-membered ring ketolactone from its spectral analyses,[12] though it could not be isolated in pure form because of its instability. These facts suggest that the oxidative cleavage of 4 goes through 8 and that 7 might be formed from the extradiol oxygenation product 9. This is probably the first example of the extradiol oxygenation of catechols in the nonenzymatic process. the intermediacy of 8 was proved by the following fact. The ruthenium-catalyzed oxygenation of the quinone 8 under similar conditions gave also 6 and 7, though the reaction rate of 8 was slower than that of 4.

The oxidation of 4 with ¹⁸O₂ revealed that the endocyclic oxygen of both 6 and 7 is undoubtedly derived from molecular oxygen. The ¹⁸O-labeled position of 6 was determined by the mass spectral analysis of 6 and the ester 10a, obtained by the methanolysis of 6.[11] It is worth pointing out that the ¹⁸O-labeled 6 could be converted into the corresponding muconic acid or its equivalent 10b, containing two ¹⁸O atoms by the hydrolysis with H₂¹⁸O, which formed together with 6 in the oxygenation of 4 with ¹⁸O₂.
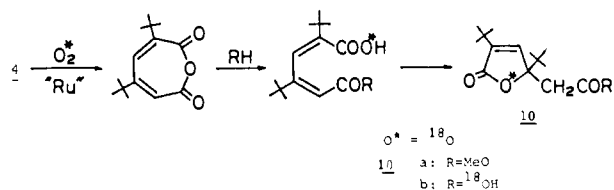
In the oxygenation described here, a ruthenium(II) complex having PPh₃ ligands was used as the catalyst. However, phosphine ligands merely supplied a ruthenium(II) catalyst that was easy to handle, but they were not essentially necessary in the oxidation of catechols. This was proved out by the following experiments.

$O^* = {}^{18}O$

10   a: R=MeO
     b: R=¹⁸OH

When a reddish brown solution of 5 in TCE was exposed to an oxygen atmosphere, its color changed immediately to dark green and the phosphine was oxidized into Ph₃PO, as James has reported.[13] It was further cleared by ³¹P NMR analysis that all the phosphine ligands were oxidized in the solution described above. In this solution, the catechol 4 was similarly oxygenated to 6 and 7.

Divalent ruthenium complexes such as RuBr₂(PPh₃)₃, Ru-(H)Cl(PPh₃)₃, Ru(H)SiClPh₂(PPh₃)₃, and Ru(H)OAc(PPh₃)₃ were also effective as the catalyst, but trivalent ruthenium such as RuCl₃ was of no use. The ratio of intradiol oxygenation to extradiol oxygenation varied with the ruthenium catalyst used. For example, Ru(H)OAc(PPh₃)₃ caused scarcely the extradiol oxygenation. The maximum turnover of the catalyst in these oxygenations was about 20 for the present.

Similar oxygenation of 4-*tert*-butylcatechol and 4-methylcatechol also gave the corresponding muconic acid anhydrides and 2*H*-pyran-2-ones. The details will be reported together with the result of the unsubstituted catechol in the near future.

Although further systematic studies are necessary to clear the mechanism of the reaction and to find a much more effective system for the oxygenation of catechol, it was made clear that ruthenium(II) catalyzed the oxygenation of catechols with molecular oxygen to yield one of the intermediates supposed in biochemical systems and to form the products of the extradiol oxygenation.

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"Open-Face" Macrobicycles as Tunable Binucleating Ligands. Design, Synthesis, and Dicopper(II) Complexes

Andrea E. Martin and John E. Bulkowski*

Department of Chemistry, Brown Chemical Laboratory
University of Delaware, Newark, Delaware 19711

Received April 3, 1981

Metal complexes of binucleating ligands are of much current interest as models[1] for active sites in metallobiomolecules and as unique bimetallic catalysts.[2] In such complexes two metal ions are positioned in close proximity by the ligand framework to promote substrate binding between them. Bimetallic complexes that are particularly attractive for studying interactions of small molecules with transition metals include those formed from binucleating macromonocycles,[3] Schiff bases,[4] "wishbones",[5]

(9) The anhydride 6 was identified by the comparison of its melting point and spectral data with those of the authentic sample prepared from 8 with *m*-chloroperbenzoic acid.[11]

(10) The pyrone 7 was obtained as colorless granules, mp 113–114 °C, from hexane. The spectral properties were as follows: ¹H NMR (CDCl₃) δ 1.19 (s, 9H), 1.26 (s, 9H), 6.01 (s, 2H); ¹H NMR (C₆D₆) δ 0.84 (s, 9H), 1.02 (s, 9H), 5.75 (d, *J* = 1.7 Hz, 1H), 5.94 (d, *J* = 1.7 Hz, 1H); ¹³C NMR (CD₂Cl₂, Me₄Si) 28.1, 29.0, 35.5, 36.2, 98.7, 107.2, 163.4, 167.7, 171.4; IR (KBr) 1710, 1630, 1550, 1255 cm⁻¹; mass spectrum (*m/z*) 208 (M⁺, 29), 180 (14), 165 (65), 151 (100).

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(12) ¹H NMR (CCl₄) δ 1.16 (s, 9H), 1.25 (s, 9H), 6.34 (br s, 1H), 6.43 (br s, 1H); ¹³C NMR (CD₂Cl₂, Me₄Si) 29.2, 29.5, 34.7, 36.7, 124.8, 134.0, 134.1, 150.0, 164.0, 190.2; IR (liquid film) 1760 and 1720 cm⁻¹; mass spectrum (*m/z*) 237 (trace, M⁺ + 1), 208 (100), 193 (85), 166 (84).

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