

Table I. Selected Bond Distances (Å) and Bond Angles (deg)

parameter	X-ray	CSD ^a	parameter	X-ray	CSD ^a
C1C2	1.488 (6)	1.515 (2)	C4C5	1.541 (7)	1.533 (2)
C1C6	1.603 (8)	1.549 (2)	C4C7	1.546 (6)	1.548 (2)
C1C7	1.570 (6)	1.551 (2)	C5C6	1.531 (9)	1.540 (3)
C1C10	1.497 (7)	1.514 (2)	C7C8	1.530 (7)	1.530 (2)
C2C3	1.476 (7)	1.519 (2)	C7C9	1.542 (6)	1.530 (2)
C2-O	1.256 (5)	1.209 (2)	C11-O	1.493 (6)	
C3C4	1.544 (6)	1.532 (2)	∠C2C1C6	98.8 (4)	103.4 (1.2) ^b

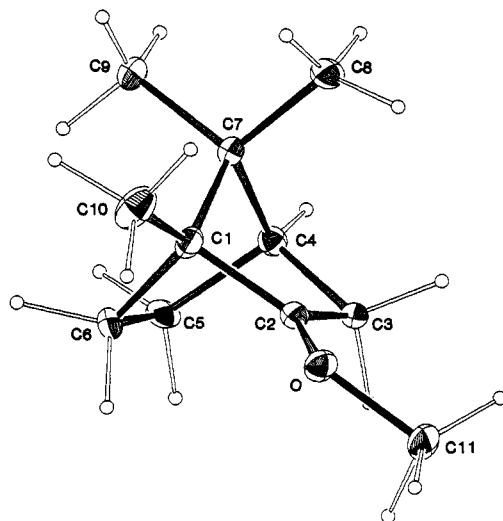
^a Camphor model, Cambridge Structural Database, ref 12. ^b Mean.

Figure 1. ORTEP drawing of 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum.

C-C distances that are several bonds removed from C2 (C7C9, C7C8, C5C6, C4C7, and C4C5) are compared with the corresponding weighted mean bond lengths of substituted camphor compounds with high quality X-ray structures¹² in Table I and are very similar.¹³ C2-O is about 0.05 Å longer than the mean camphor carbonyl distance;¹² it is, nonetheless, at least 0.1 Å shorter than the typical C-O length in ethers,¹⁴ indicating predominant oxonium ion character. For a methoxy group attached to a positive carbon 1.256 (5) Å is reasonable.⁴ The C-C bonds near the cationic center are the most interesting; C1C6 is highly abnormal. At 1.603 (8) Å it is one of the relatively few single bonds that is over 1.60 Å.¹⁵ This is 0.05 Å longer than the average value in simple bicyclo[2.2.1]heptanes¹³ or the camphor model.¹² The remaining structural units in the vicinity of C2 are altered in a less dramatic fashion. Notably, C1C2, C2C3, and C1C10 appear to be on the short side, whereas C1C7 is slightly long.¹² A plausible explanation for the considerable lengthening of C1C6 is carbon-carbon hyperconjugation, although alternative explanations are conceivable.¹⁶ The "vacant" orbital on C2 and the C1C6 bond are properly aligned for such an effect. The dihedral angle formed by C1C6, C1C2, and a line perpendicular to the C1C2C3-O plane at C2 is about 18°. The quantitative pattern of the neighboring parameters is also compatible with this interpretation. Because of the presence of the strongly electron-releasing methoxy group, it is somewhat surprising that C1C6 is in the same general range (1.62 (2) Å) as the C_αC_β bonds in the 3,5,7-trimethyladamantyl carbenium ion.¹⁷ A final point

worth noting is that the nonbonded distance between C2 and C6 is 2.35 Å (∠C2C1C6 = 98.8 (4)°), which is 0.05 Å shorter than the mean C2...C6 camphor distance¹² (∠C2C1C6 = 103.4 (1.2)°). This could reflect slight bridging by C6, although some reduction in C2...C6 is expected because of the decreased electron density at C2.

The major contribution of our study is to provide a reliable structural benchmark to be used in spectroscopic, thermodynamic, kinetic, and theoretical comparisons. It has been suggested that hyperconjugation and bridging are related rather than independent phenomena.¹⁸ Moreover, it has been stated¹⁹ that there should be a bonding continuum in 2-norbornyl cations ranging from hyperconjugation without significant motion toward bridging, to unsymmetrical bridging,^{20,21} to symmetrical bridging. Crystal structures of less drastically functionalized²⁰ norbornyl systems and the parent carbocation now appear feasible and will afford a rigorous basis for testing the above proposals.

Supplementary Material Available: Cell parameters, fractional coordinates, thermal parameters, bond distances, and bond angles of 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum (4 pages). Ordering information is given on any current masthead page.

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(19) Reference 1f; p 161.

(20) Several individuals have informed us that a structure of 1,2,4,7-anti-tetramethyl-2-norbornyl cation has been obtained and accepted for publication (ref 21). The carbocation is reportedly unsymmetrically bridged with C1C6 = 1.74 Å!

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Biomimetic Aerobic 1,4-Oxidation of 1,3-Dienes Catalyzed by Cobalt Tetraphenylporphyrin-Hydroquinone-Palladium(II). An Example of Triple Catalysis

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The use of macrocyclic metal complexes, in particular metalloporphyrins, as biomimetic catalysts in oxidation reactions has attracted considerable attention recently.²⁻⁷ Most of the me-

(11) Cambridge Structural Database (CSD), 47 structures, mean B-F = 1.350 (23) Å.

(12) Camphor model, CSD, 10 structures, weighted mean parameters.

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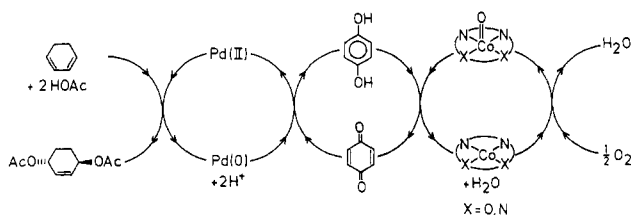
(16) Reference 1f; Chapter 14.

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(1) Correspondence to this author can be made at the University of Uppsala.

(2) For a review, see: Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578.(3) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) Groves, J. T.; Kruper, W. J.; Haushalter, R. S. *Ibid.* **1980**, *102*, 6375. (c) Hill, C. L.; Schardt, J. A. *Ibid.* **1980**, *102*, 6374.(4) (a) Guilmet, E.; Meunier, B. *Tetrahedron Lett.* **1980**, *21*, 4449. (b) De Carvalho, M. E.; Meunier, B. *Tetrahedron Lett.* **1983**, *24*, 3621.(5) De Poorter, B.; Ricci, M.; Meunier, B. *Tetrahedron Lett.* **1985**, *26*, 4459.(6) (a) Renaud, J. P.; Battioni, P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1985**, 888. (b) Mansuy, D.; Bartoli, J. F.; Momenteau, M. *Tetrahedron Lett.* **1982**, *23*, 2781.

Scheme I

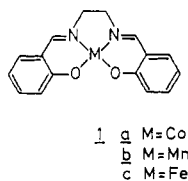


talloporphyrins used have utilized oxidants such as iodosylbenzene,³ hypochlorite,⁴ persulfate,⁵ and peroxide.⁶ There are only a few examples⁷ of the use of molecular oxygen as the ultimate oxidant, and in these systems, except in one case,^{7c} a reductive activation of dioxygen is needed.

During our work on the use of *p*-benzoquinone/hydroquinone as a catalytic electron carrier in oxidation reactions,⁸⁻¹⁰ it occurred to us that a combination of a macrocyclic metal complex and *p*-benzoquinone/hydroquinone would constitute an interesting electron-transfer system for oxidation reactions. We report here on a catalytic system for O₂ oxidation involving a multistep electron transfer with the three redox couples Pd(II)/Pd(0)-*p*-benzoquinone/hydroquinone-(oxo)Co(TPP)/Co(TPP) as catalysts.

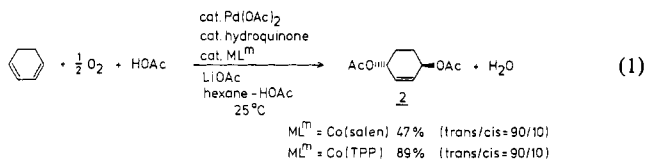
Benzoquinones are well-known oxidants in synthetic organic chemistry,¹¹ and we have recently used benzoquinones as oxidants and electron carriers in selective palladium-catalyzed oxidations of conjugated dienes.⁸⁻¹⁰ One important goal in these reactions is to find a rapid and mild system for reoxidation of hydroquinone to benzoquinone by molecular oxygen. It has been reported in the literature that catechols and *p*-hydroquinones can be oxidized to quinones by molecular oxygen in the presence of Co(salen) (**1a**), Mn(salen) (**1b**), Fe(salen) (**1c**), or cobaloxime derivatives.^{12,13}

In a first attempt to obtain an oxygen-based reoxidation of hydroquinone in our catalytic reactions we tried to use the salen complexes **1** as catalysts. Reaction of 1,3-cyclohexadiene with



O₂ (1 atm) at 25 °C in a biphasic system of hexane and acetic acid in the presence of LiOAc and catalytic amounts of Pd(OAc)₂, hydroquinone, and Co(salen) resulted in a selective oxidation to yield *trans*-1,4-diacetoxy-2-cyclohexene (**2**) (eq 1). The rate was linearly dependent on Co(salen) in the range of 3–9 mol % of the complex. The use of 9 mol % of Co(salen), 5 mol % of Pd(OAc)₂, and 15 mol % of hydroquinone afforded a 47% yield of **2** after 35 h.

The principle for this catalysis is shown in Scheme I. It consists of three different catalytic cycles. These redox cycles schematically show the redox processes involved. The formation of palladium(0) is only in a formal sense, since metallic palladium is never formed.¹⁴



The corresponding reactions using Mn(salen) (**1b**) or Fe(salen) (**1c**) in place of Co(salen) (**1a**) were very slow and gave <5% yield after 50 h.

In the Co(salen) system the rate-limiting step was found to be the reoxidation of hydroquinone to benzoquinone by O₂/Co(salen). This may be either a result of an inefficient uptake of oxygen by Co(salen) to give a low concentration of the oxygen complex or a result of a slow electron transfer from hydroquinone to the cobalt-oxygen complex. To investigate this point we studied the rate of oxidation of 1,3-cyclohexadiene as a function of the oxygen pressure. The reaction rate at 1, 3, and 5 atm of O₂ was found to be approximately the same, indicating that the major part of the cobalt is in the form of an oxygen complex and that the electron transfer from hydroquinone to that complex is slow.

We therefore investigated some other macrocyclic metal complexes.¹⁵ Metalloporphyrins have been reported to catalyze many O₂ oxidations, and in particular cobalt and manganese porphyrins are known to catalyze the oxidation of phenols to quinones by molecular oxygen.^{12b} We first tried Co(II)(TPP) (TPP = *meso*-tetraphenylporphyrin¹⁶). It was found that this complex catalyzed a fast and efficient electron transfer to the dioxygen in the palladium-hydroquinone-catalyzed oxidation of the diene. Thus, the oxidation of 1,3-cyclohexadiene by O₂ (1 atm) using 5 mol % each of Co(TPP), hydroquinone, and Pd(OAc)₂ afforded an 89% isolated yield of **2** within 18 h at 25 °C (eq 1). The selectivity for 1,4-diacetate was >95%. In contrast to the Co(salen) case, the rate of the oxidation was not significantly dependent on the concentration of Co(TPP). This indicates that the electron transfer from hydroquinone to the oxygen complex as well as the oxygen uptake by Co(TPP) are efficient processes. A mechanism of this biomimetic triple catalysis is indicated in Scheme I.¹⁷ No oxidation occurred in the absence of any of the three catalysts. In a typical experiment, Co(TPP) (50 mg, 0.07 mmol), LiOAc·2H₂O (163 mg, 1.60 mmol), and hydroquinone (8 mg, 0.07 mmol) in acetic acid (2.5 mL). To the resulting slurry was added a solution of 1,3-cyclohexadiene (120 mg, 1.5 mmol) in *n*-hexane (5 mL). The reaction was stirred at room temperature under 1 atm of O₂ for 18 h. The precipitate was removed by filtration, and the hexane phase was collected. The remaining acetic acid phase was diluted with saturated aqueous NaCl (3 mL) and extracted with hexane/ether (1:1) (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl (3 × 3 mL), water (3 × 3 mL), and finally 2 M NaOH (3 × 5 mL). The organic phase was dried (MgSO₄) and evaporated to yield 264 mg (89%) of **2** (>90% trans) as crystals.

A few other conjugated dienes were tested and oxidized to 1,4-diacetoxy-2-alkenes by using the palladium-hydroquinone-Co(TPP) system. The results parallel the results from the previously investigated palladium-catalyzed 1,4-diacetoxylation,⁹ where the ultimate oxidant was manganese dioxide (with catalytic

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(14) The reaction proceeds via a (π -allyl)palladium(benzoquinone) complex (see ref 9a). It is not clear whether palladium(II) and hydroquinone are instantaneously formed during the nucleophilic attack by acetate or if a palladium(0)-(benzoquinone) complex is first formed, which then decomposes to palladium(II) and hydroquinone.

(15) The use of the pyridine complex of bis(dimethylglyoximate)cobalt(II) (cobaloxime) as catalyst gave no oxidation product in acetic acid. This complex is known to catalyze the oxidation of hydroquinone to *p*-benzoquinone by molecular oxygen in acetone.¹³

(16) This ligand was synthesized in 16% yield by the condensation of benzaldehyde and pyrrole in propionic acid in the presence of zinc acetate according to Momenteau et al.: Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perkin Trans 1* **1983**, 189.

(17) The oxocobalt(IV) complex shown is drawn only to formally represent the oxidized form of Co(TPP). At present, very little information regarding the mechanism of the O₂-Co-quinone couple is available, and other oxygenated complexes such as superoxo compounds may be involved.

amounts of *p*-benzoquinone). For example, the oxidation of 1,3-cycloheptadiene by O₂ in acetic acid (2 M on LiOAc) at 40 °C catalyzed by 5 mol % each of Co(TPP), hydroquinone, and Pd(OAc)₂ afforded *cis*-1,4-diacetoxy-2-cycloheptene (>92% *cis*) in 65% isolated yield.

The corresponding oxidation using Mn(TPP) in place of Co(TPP) also worked but was considerably slower. For example, the oxidation of 1,3-cyclohexadiene gave only a 56% yield of 1,4-diacetoxy-2-cyclohexene after 48 h, and now the *trans/cis* ratio was only 72/28.

The oxidation described here has similarities with biochemical processes where an oxidation becomes very mild and selective when several redox couples with falling redox potentials are interacting. In many biological systems metalloporphyrins and *p*-hydroquinones/*p*-benzoquinones play important roles as electron carriers. For example, ubiquinones are known to mediate the electron-transfer processes involved in energy production in aerobic organisms. The model system described here is to our knowledge the first example of a selective oxidation using a triple catalysis with oxygen as the ultimate oxidant.

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Registry No. Co(TPP), 14172-90-8; Pd, 7440-05-3; O₂, 7782-44-7; hydroquinone, 123-31-9; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0.

Enantioselective Ring Construction through Asymmetric Olefin-Ketene Cycloaddition. A Highly Enantiocontrolled Approach to (–)-α-Cuparenone and (+)-β-Cuparenone

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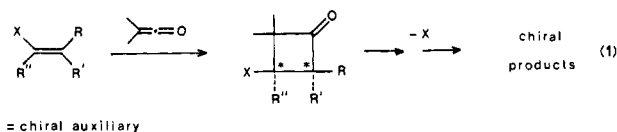
Chiral auxiliary-mediated reactions that manifest high levels of diastereoselection represent valuable sources of enantiomerically enriched synthetic intermediates.¹ The asymmetric Diels-Alder reaction has proven particularly useful for this purpose and has been effectively applied in numerous enantioselective natural product syntheses.^{1,2} In surprising contrast, the potential in asymmetric synthesis of the versatile [2 + 2] cycloaddition reaction of olefins with ketenes,³ which also offers an excellent possibility for auxiliary-directed π -face stereoselection,⁴ has yet to be demonstrated. In this communication we wish to report the first example of the use of chiral olefin-ketene diastereofacial differentiation for enantioselective natural product synthesis (eq 1).

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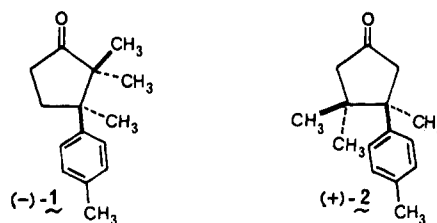
(2) For reviews of the asymmetric Diels-Alder reaction in organic synthesis, see: Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876-889. Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986; Vol. 4, pp 261-306.

(3) See: Brady, W. T. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1980; Chapter 8. Brady, W. T. *Tetrahedron* **1981**, *37*, 2949-2966, and references cited therein.

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α- and β-Cuparenones (**1** and **2**), deceptively simple sesquiterpenes from the essential oil of *Mayur pankhi* and the liverwort *Mannia fragrans*,⁵ have often been synthesized in racemic form



(–)-α-Cuparenone

(+)-β-Cuparenone

to illustrate new procedures for cyclopentanone construction and/or methods for juxtaposing quaternary centers.^{6,7} Our enantioselective chiral olefin-dichloroketene based common approach to these model cyclopentanoid natural products will serve both to indicate the excellent level of chiral induction that can attend this cycloaddition process and to show some of the significant latent flexibility⁸ that resides in the cyclobutanones so obtained.

The allylic chloride **3**⁹ was transformed with readily available, optically pure (1*S*,2*R*)-(+)-2-phenylcyclohexanol¹⁰ (0.6 equiv, 1.2 equiv of NaH, THF, 90%) to the chiral allylic ether (+)-**4**¹¹ (Scheme I), which on contact with 1.6 equiv of sublimed potassium *tert*-butoxide in dimethyl sulfoxide¹² at 65 °C afforded in 75% yield and with essentially complete stereoselectivity the *E* enol ether (–)-**5**.¹¹

Our expectation that (–)-**5** would enter into reaction with dichloroketene through a favorable π -face discriminating transition-state conformation was based on steric considerations. For steric reasons, (–)-**5** was expected to adopt the *s*-*trans* (or nearly *s*-*trans*) conformation depicted,¹³ which would effectively bare

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(11) (+)-**4**: mp 72-74 °C, [α]_D²¹ +32° (c 1.0, CHCl₃); (–)-**5**: mp 60-61 °C, [α]_D²¹ –80° (c 1.1, acetone); (–)-**6a**: mp 89-90 °C, [α]_D²¹ –57° (c 1.1, CHCl₃); (+)-**7**: mp 42-44 °C, [α]_D²⁰ +71° (c 1.7, CHCl₃); (–)-**8**: mp 57-60 °C, [α]_D²⁰ –66° (c 1.7, CHCl₃); (+)-**9**: [α]_D²⁰ +253° (c 1.7, CHCl₃); (–)-**1**: mp 50-51 °C (lit.^{5a} mp 52-53 °C), [α]_D²¹ –170° (c 0.2, CHCl₃); (+)-**2**: [α]_D²⁹ +45° (c 1.4, CHCl₃).

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