

phenoxide concentration was determined from UV/Vis spectroscopy at 288 nm (phenol), 390 nm (3-nitrophenol), 400 nm (4-nitrophenol), or 420 nm (2,4-dinitrophenol), within the linear Beer's Law regime as determined by a four-point calibration curve. For quantitation in THF, the matrix was heated at reflux in the absence of air with 1 equiv of nitrophenol in THF (4 mL) for 2 h. The concentration of phenoxide was measured spectroscopically as above.

Size-exclusion experiments. The cross-linked LLC matrix (10 mg) was stirred with 1 equiv, by cation content, of either Alcian Blue (pyridine variant) or gallamine triethiodide in D₂O (2 mL) in the absence of air. After one day of stirring, the suspensions were centrifuged and an aliquot was analyzed. Alcian Blue (pyridine variant) was analyzed quantitatively by UV/Vis spectroscopy at 615 nm. Measurements were taken within the linear regime for Beer's Law. Gallamine triethiodide concentrations were analyzed by integration of ¹H NMR signals using DMSO as an internal standard.

Received: May 17, 1999 [Z13430IE]

German version: *Angew. Chem.* **1999**, *111*, 3206–3210

Keywords: heterogeneous catalysis • liquid crystals • nanostructures • zeolite analogues

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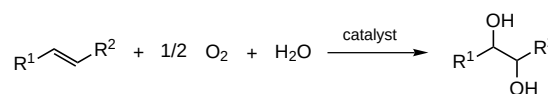
Atom-Efficient Oxidation of Alkenes with Molecular Oxygen: Synthesis of Diols**

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Dedicated to Professor Manfred Baerns on the occasion of his 65th birthday

The selective oxidation of alkenes with molecular oxygen involving the participation of both oxygen atoms is one of the most significant challenges in modern catalysis research. In spite of the advantages of oxygen over “classical” stoichiometric oxidizing agents (e.g. peracids, chlorates, periodates), only one oxygen atom is generally incorporated into the molecule in the oxidation of alkenes with molecular oxygen. The second oxygen atom reacts with a reducing agent present to form by-products, which are thus formed in stoichiometric amounts. Such processes are found in enzymatic oxidations,^[1] transition metal catalyzed reactions with O₂/H₂, and stoichiometric reactions with O₂/RCHO or O₂/alkylarenes.^[2] Groves et al. have been able for the first time to show that both oxygen atoms of molecular oxygen are used during epoxidation in the presence of a porphyrin–ruthenium catalyst.^[3]

Because of the industrial importance of diols, both as bulk chemicals (in particular propylene glycol)^[4] and as fine chemicals, we are interested in carrying out dihydroxylations with molecular oxygen as oxidant (Scheme 1).



Scheme 1. Metal-catalyzed dihydroxylation with molecular oxygen.

Osmium(VIII) compounds have proved to be the most reliable metal catalysts for dihydroxylations. On the basis of the pioneering work of Sharpless et al.^[5] it has been possible to demonstrate the preparative potential of the method,

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[**] This work was supported by the Bildungsministerium des Landes Mecklenburg-Vorpommern and Bayer AG (Leverkusen). We thank I. Stahr for experimental support, and K. Kortus and Dr. C. Fischer for the GC and HPLC investigations.

Table 1. Dihydroxylation of 1-octene.^[a]

Entry	pH	Ligand	Os:L	Conversion [%]	Sel. [%]	Yield [%]	ee [%]
1	7	–	–	13	4	< 1	–
2	9	–	–	69	83	57	–
3	10.4	–	–	91	89	81	–
4	11.2	–	–	63	72	46	–
5	10.4	DABCO ^[b]	1:1	96	97	92	–
6	10.4	DABCO	1:3	99	97	96	–
7	10.4	quinuclidine	1:3	99	96	95	–
8	10.4	(DHQD) ₂ PHAL ^[c]	1:3	99	98	98	65 (R)
9	10.4	(DHQ) ₂ PHAL ^[d]	1:3	99	96	97	54 (S)

[a] In all reactions 1-octene (2.0 mmol) was allowed to react in the presence of 0.5 mol % K₂[OsO₂(OH)₄] in a mixture of aqueous buffer solution (25 mL, phosphate buffer with the given pH value) and *tert*-butyl alcohol (10 mL) at 1 bar O₂ and 50 °C with stirring (reaction time 14–18 h). [b] DABCO = 1,4-diazabicyclo[2.2.2]octane. [c] (DHQD)₂PHAL = hydroquinidine 1,4-phthalazinediyl diether.^[6] [d] (DHQ)₂PHAL = hydroquinine 1,4-phthalazinediyl diether.^[6]

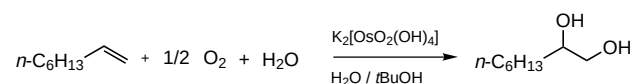
Table 2. Dihydroxylation of different alkenes with oxygen.^[a]

Entry	Alkene	Ligand ^[b]	Cat. [mol %]	Conversion [%]	Sel. [%]	Yield [%]	ee [%]
1	vinyl naphthalene	DABCO	1	75	75	56	–
2	vinyl naphthalene	(DHQD) ₂ PHAL	1	72	76	55	96 (R)
3	styrene	DABCO	2	66	77	51	–
4	styrene	(DHQD) ₂ PHAL	2	67	78	52	90 (R)
5	α -methylstyrene	DABCO	0.5	100	97	97	–
6	α -methylstyrene	(DHQD) ₂ PHAL	0.5	100	96	96	80 (R)
7	1-phenylcyclohexene	DABCO	2	90	95	85	–
8	1-phenylcyclohexene	(DHQD) ₂ PHAL	2	53	96	51	86 (R,R)
9	cyclohexene	DABCO	0.5	90	75	68	–

[a] The alkene (2.0 mmol) was allowed to react in the presence of K₂[OsO₂(OH)₄] in a mixture of aqueous buffer solution (25 mL, pH 10.4) and *tert*-butyl alcohol (10 mL) at 1 bar O₂ and 50 °C with stirring (reaction time 16–24 h). [b] Ratio osmium/ligand = 1/3.

especially in asymmetric catalysis.^[6] In contrast, investigations on the use of molecular oxygen as oxidant for osmium-catalyzed dihydroxylations have been largely ignored,^[7] especially since in 1968 Cairns et al. demonstrated that diols were not formed during osmium-catalyzed dihydroxylations in the presence of oxygen.^[7a] More recent work by Krief et al. has shown with the example of the dihydroxylation of α -methylstyrene that such a reaction is possible, however, by light induction in the presence of sensitizers (8 mol % arylselenides).^[8]

We describe here for the first time highly selective (chemo- and enantioselective) osmium-catalyzed dihydroxylations of alkenes which can be carried out simply with molecular oxygen without the addition of cocatalysts, even under mild conditions. With the backdrop of the industrial importance of aliphatic diols^[9] we chose the transformation of 1-octene as model reaction (Scheme 2 and Table 1). Since the oxidative



Scheme 2. Dihydroxylation of 1-octene.

action of the Os/O₂ system is highly dependent upon the pH value of the reaction medium,^[7a] we first investigated the dihydroxylation of 1-octene in different aqueous buffer systems. To overcome the problem of further, nonselective oxidation of the diols, an organic solvent was added so that a second phase was formed under the reaction conditions.

As Table 1 shows (entry 1), no significant diol formation is observed at pH 7. In contrast, in the basic pH range (optimum: pH 10.4) osmium is reoxidized to active dihydroxylation catalysts (entries 2 and 3). At higher pH values the chemoselectivity of the reaction falls (entry 4). The oxygen consumption measured, which is almost 1 mmol for 2 mmol of substrate, shows that both oxygen atoms are used productively in the oxidation reaction. Since osmium-catalyzed dihydroxylation is a ligand-accelerated reaction (“ligand-accelerated catalysis”),^[10] the chemoselectivity of the catalyst should be improved by the addition of ligand. Indeed, higher yields are obtained by the addition of 1.5 mol % 1,4-diazabicyclo[2.2.2]octane (DABCO) or 1.5 mol % quinuclidine as ligands (entries 6 and 7). Thus, 1-octene is oxidized to 99 % after 18 h in the presence of 0.5 mol % Os, and 1,2-octanediol is obtained with 97 % selectivity. To the best of our knowledge this is the highest selectivity obtained in transition metal catalyzed oxidation of alkenes with molecular oxygen.

The stereoselective dihydroxylation of 1-octene was also achieved with the use of chiral quinine and quinidine ligands developed by Sharpless et al.^[5] (entries 8 and 9). We explain the somewhat lower enantioselectivities compared to dihydroxylations with K₃[Fe(CN)₆] as oxidant by the higher reaction temperatures in our system and the competition of hydroxide ions as ligands for the central metal.

Next we dihydroxylated different alkenes under the reaction conditions optimized for 1-octene. The results are summarized in Table 2.

In addition to aliphatic alkenes with a terminal double bond we investigated arylalkenes (styrene, vinyl naphthalene), the

1,1-disubstituted alkene α -methylstyrene, the 1,2-*cis*-disubstituted alkene cyclohexene, and the trisubstituted alkene 1-phenylcyclohexene. In all cases diol selectivities of over 75% are obtained, frequently greater than 90%. Calculations of oxygen consumption show that in all reactions both oxygen atoms are used productively for diol formation and catalyst regeneration. The aryl-substituted diols are formed with good to very good enantioselectivities (80–96% *ee*) which are only slightly lower than those achieved under the optimized Sharpless conditions. This is largely attributable to the higher temperature (50°C compared to 0°C).

In summary, osmium-catalyzed dihydroxylations may be carried out simply and practicably with oxygen at normal pressure in a basic two-phase system. Both oxygen atoms are incorporated into the product in an atom-efficient manner. The diols are obtained in excellent yields, and the catalyst can be recycled. Thus the method described here represents not only an improvement over the versatile Sharpless dihydroxylation, but also opens up new perspectives for by-product-free preparation of diols used on an industrial scale.

Received: June 22, 1999 [Z13598]

German edition: *Angew. Chem.* **1999**, *111*, 3211–3212

Keywords: dihydroxylations • homogeneous catalysis • osmium • oxidations • oxygen

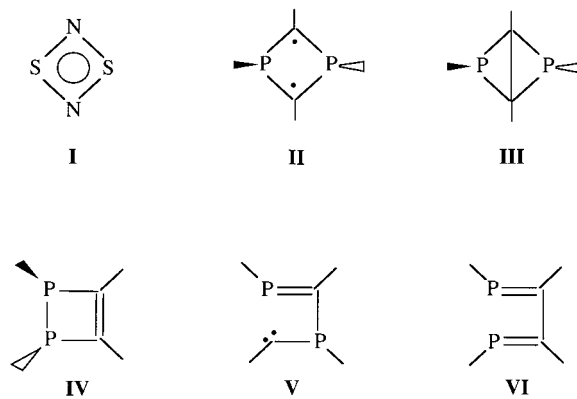
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Valence Isomerization of a 1,3-Diphosphacyclobutane-2,4-diyl: Photochemical Ring Closure to 2,4-diphosphabicyclo[1.1.0]butane and Its Thermal Ring Opening to *gauche*-1,4-Diphosphabutadiene**

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Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

The disulfur dinitride **I** is generally considered as a prominent example of an electron-rich π -delocalized four-membered ring system.^[1] Valence isomerization to a bicyclobutane, butadiene, or cyclobutene analogue is unknown, although polymerization by means of diradical ring opening is known.^[2] Recently, we established^[3] the existence of a further four-membered ring system, isoelectronic with **I**, in the form of 1,3-diphosphacyclobutane-2,4-diyl **II** (a 2,4-diphosphabicyclo[1.1.0]butane bond stretch isomer^[4]) and characterized structurally the first derivatives.^[3, 5] Ab initio calculations confirm a substantial diradical contribution to the parent system of **II**^[6] which results from the high inversion barrier of the phosphorus atom. Transannular C–C bond formation to the thermodynamically favored 2,4-diphosphabicyclo[1.1.0]butane **III**,^[7] however, does not occur.^[8] Instead, thermal rearrangements are induced which, similar to **I**, were initiated by ring opening.^[3, 5] This includes the valence isomerization of **II** to 1,2-dihydro-1,2-diphosphete **IV** which we recently reported,^[9] and which proceeds via a phosphanylcarbene **V**.^[10] We report here on the photochemically induced ring closure of **II** to the 1,3-diphosphabicyclo[1.1.0]butane **III** and its thermal ring opening to *gauche*-1,4-diphosphabutadiene **VI**. Previously, phosphabicyclobutanes have only been known with phosphorus in the bridge position,^[11] for free phosphabutadienes only the *trans* form has been hitherto established.^[12]



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[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie. Published in part at the "XIV International Congress on Phosphorus Chemistry", Cincinnati, **1998**, Abstr. No. LM 2-3.