

ORGANIC SELENOXIDES AS OXIDANTS IN
OSMIUM TETROXIDE CATALYZED OXIDATION OF
OLEFINS TO GLYCOLS

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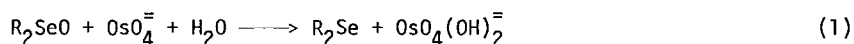
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SUMMARY: Olefins are catalytically oxidized to glycols by osmium tetroxide in the presence of organic selenoxide cooxidants. Glycols were obtained in good yields from mono-, di-, tri- and tetrasubstituted olefins.

Osmium tetroxide is widely used as a catalyst for the cis-dihydroxylation of olefins in conjunction with stoichiometric cooxidants such as hydrogen peroxide, metal chlorates, and *t*-butyl hydroperoxide (1). Oxygen as a stoichiometric oxidant in osmium tetroxide catalyzed dihydroxylation of olefins has been patented (2), but apparently low reaction rates and rapid catalyst deactivation diminish the practical utility of the method.

We report on our investigation of novel homogeneous, liquid phase, olefin oxidation systems composed of osmium, cooxidant, and oxygen. The cooxidant cycles the reduced osmium catalyst and the cooxidant, in turn, is recyclable with oxygen.

We found that organic selenoxides are effective cooxidants in osmium tetroxide catalyzed olefin to glycol reactions. Alkaline solutions of diphenyl- and phenylmethyl selenoxide in alkaline aqueous acetone, oxidize soluble osmium (VI) to osmium (VIII). The selenoxide is cleanly reduced to the selenide (Eq. 1).



Alkaline solutions of the two selenoxides containing catalytic quantities of osmium tetroxide are stable over a period of hours. When they are combined with a variety of olefins,

1,2-diols form in good yields (Table). Based on the yield of glycol, at least 100 catalyst turnovers have been obtained, and there is no evidence of irreversible catalyst deactivation.

TABLE
OSMIUM TETROXIDE - DIORGANYL SELENOXIDE OXIDATION OF OLEFINS^a

Olefin	Selenoxide	Product	Yield, % ^b
Ethylene	Diphenyl Selenoxide	Ethylene glycol	80
Propylene	"	Propylene glycol	95
Cyclohexene	"	<u>cis</u> -1,2-cyclohexanediol	63
1-Methylcyclohexene	"	1-Methyl- <u>cis</u> -1,2-cyclohexanediol	30 ^c
2,3-Dimethyl-2-butene	"	2,3-Dimethyl - 2,3-butanediol	54 ^c 98 ^d
Ethylene	Phenylmethyl Selenoxide	Ethylene glycol	77
Propylene	"	Propylene glycol	85

a Solvent: acetone - 0.1 N K₂CO₃ 1:1

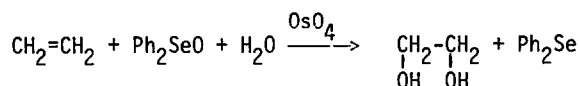
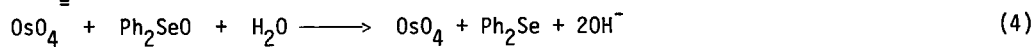
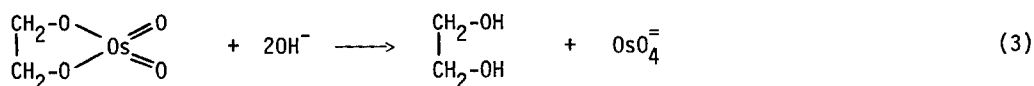
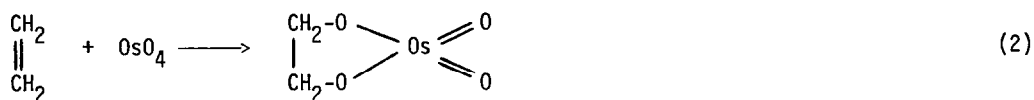
b Yields, determined by GC using an internal standard, are based on the amount of diphenyl selenoxide.

c Unreacted selenoxide remains after 24 hr reaction time at room temperature.

d Reaction temperature 50°C; reaction time 24 hr.

Although the oxidation mechanism is unknown, the sequence of reactions in the Scheme below is attractive on the basis of equation 1 and because selenoxides fail to oxidize osmium VI when it is present as an osmate ester in neutral organic solvents.

Scheme



The slow step in the overall oxidation of unhindered olefins seems to be the formation of the osmate ester (Eq. 2). This is in agreement with the observation that ethylene which is less nucleophilic than propylene, reacts slower than propylene with osmium tetroxide. Hindered olefins (Table), react much more slowly than ethylene or propylene. This suggests that the rate determining step is the hydrolysis of the sterically crowded osmate ester (Eq. 3). Relatively stable diosmate esters have been reported by Griffith (3).

Diorganyl selenoxides are mild oxidants (4) that function by oxygen atom transfer. When used as cooxidants with osmium tetroxide for olefin dihydroxylation, no oxidation of the product glycols to α -ketols is observed. Less water soluble, higher molecular weight olefins can be oxidized at good rates, since the selenoxides are soluble in organic-aqueous solvents without loss of oxidizing ability. Using diorganyl selenoxides as oxidants is attractive because they can be cleanly made by singlet oxygen oxidation of the selenides (5), and can therefore act in a catalytic fashion as singlet oxygen transfer agents.

We found via a modified literature procedure (5), that phenylmethyl selenide is efficiently oxidized to the corresponding selenoxide with photochemically generated singlet oxygen under conditions suitable for osmium tetroxide-selenoxide olefin oxidation. Thus, using catalytic amounts of both the organic selenide and osmium tetroxide, cyclohexene was converted to cis-1,2-cyclohexanediol using photochemically generated singlet oxygen as the oxidant (see Experimental). The two main free radical oxidation products cyclohex-2-ene-1-ol and cyclohex-2-ene-1-one were also formed in small amounts. A control experiment in the absence of selenide and sensitizer gave also cis-1,2-cyclohexanediol as the main product in accordance with the literature (2), but the catalyst deactivated rapidly and gave much lower turnover numbers. It should be recognized that with the sensitized system the recycling of the reduced osmium may be achieved by the in situ formed selenoxide, but also by the singlet oxygen itself or even by the singlet oxygen olefin oxidation products.

EXPERIMENTAL: All operations were conducted in a well-ventilated hood; rubber gloves were used to avoid contact with the toxic osmium tetroxide. Excess reagents were reduced with sodium sulfite before disposal.

Oxidation of Olefins by Selenoxides - Osmium Tetroxide. General Procedure*

A 100 ml-round bottom three-neck flask equipped with magnetic stirring bar, thermometer, reflux condenser and dropping funnel was charged with a solution of 20 m moles of the appropriate organic selenoxide in 40 ml acetone - 0.1 N K_2CO_3 (1:1). Osmium tetroxide (0.63 ml, 0.1 m moles, of a 4% solution in 0.1 N K_2CO_3) was added with a syringe followed by dropwise addition of 25 m moles of the olefin. Cloudiness developed soon, and eventually a layer of oily selenide separated. The consumption of selenoxide (and the progress of the reaction) was followed by tlc analysis. The mixture was stirred overnight at room temperature and was then treated with 10 ml of 10% aqueous $NaHSO_3$ to reduce both remaining selenoxide and

osmium tetroxide. The mixture was transferred to a separatory funnel, and the layer of selenide was separated. The water-acetone layer was extracted with ether, washed with saturated brine, dried over MgSO_4 and concentrated to afford the crude diol.

Osmium Tetroxide-Phenylmethyl Selenide Catalyzed Oxidation of Cyclohexene by Photochemically Generated Singlet Oxygen

A 100 ml Fischer-Porter glass pressure reactor was charged with a solution of 0.171 g (1.0 m moles) phenyl methyl selenide, and 5 mg rose Bengal in 70 ml 1:1 acetonitrile-0.1 N potassium carbonate, and was pressurized with 50 psi of oxygen. The reactor was irradiated with two 200 watts incandescent light bulbs for 60 min. The oxygen was vented, and osmium tetroxide (0.8 ml of a 4% solution in 0.1 N potassium carbonate) was added followed by 2 ml (20 m moles) of cyclohexene. The reactor was repressurized with 50 psi of oxygen and irradiated. Oxygen was continuously consumed. After 2.5 hrs. 10.4 m moles of 1,2-cyclohexanediol had been formed.

ACKNOWLEDGEMENTS

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*The procedure applies to liquid olefins. For gaseous olefins a Fischer-Porter glass pressure reactor is used and the progress of the reaction is followed by the olefin pressure drop.

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