

# Epoxidation of cyclooctene and cyclohexene with hydrogen peroxide catalyzed by bis[3,5-bis(trifluoromethyl)-diphenyl] diselenide: Recyclable catalyst-containing phases through the use of glycerol-derived solvents

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## ABSTRACT

A green strategy has been explored for olefin epoxidation which combines renewable solvents (derived from glycerol), aqueous hydrogen peroxide, and catalyst recycling (a seleninic acid derivative). The use of fluorinated glycerol derivatives allows good catalytic activity in the epoxidation of cyclooctene and cyclohexene with aqueous hydrogen peroxide, preventing epoxide hydrolysis to a great extent, which is particularly remarkable in the case of cyclohexene. Furthermore, recycling of the catalytically active phase is possible through distillation of the cyclohexene oxide from the reaction mixture, which can be subsequently recharged with fresh oxidant and substrate.

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## 1. Introduction

Olefin epoxidation is a key transformation in organic synthesis both on a laboratory and on industrial scale, due to the interest of epoxides in the production of chemicals and fine chemicals [1]. The use of hydrogen peroxide for selective epoxidations is highly desirable because it is cheap, the active oxygen content is high, and it is clean, since the only by-product formed is water [2]. Many catalytic systems based on different metals have been reported for the epoxidation of a wide range of alkenes using hydrogen peroxide [3–5].

Peroxyseleonic acids were first used as stoichiometric oxidants [6], but following the discovery by Umbreit and Sharpless [7] that *tert*-butyl hydroperoxide can be used in conjunction with catalytic amounts of those selenium derivatives, the method gained interest [8]. Further improvements came with the use of hydrogen

peroxide instead of *tert*-butyl hydroperoxide as the oxidant and the heterogenisation [9,10] and functionalisation of the aromatic ring of the selenium catalyst with the electron withdrawing nitro-substituents [11–13].

Applications of selenium reagents in organic chemistry have developed rapidly over the past years, and comprehensive reviews on this area have appeared [14–20]. Moreover diselenides can be easily oxidized *in situ* by hydrogen peroxide to seleninic acid or peroxyseleonic acid, which are in some cases excellent catalysts in the oxidation of organic compounds [21–24], as, for instance, epoxidation reaction of alkenes [25], Baeyer–Villiger reaction [26], oxidation of carbonyl compounds [27], dehydrogenation of carbonyl compounds [28,29], oxidation of secondary amines [30,31], oxidation of imines [32], or selenenylations or halogenations [33].

But there are other many applications for selenium, for instance organoselenium ligands have been used for metal-catalyzed processes [34], it has been recently included in polyoxometalates to generate a new active catalyst for the epoxidation of olefins [35], or some selenium derivatives have potential as efficient mimetics for selenoenzymes [36].

The efficiency of any catalytic reaction can be further improved by catalyst recycling, which is usually accomplished by using solid heterogeneous catalysts. However, the use of classical heterogeneous catalysts (for instance, those based on titanium) together

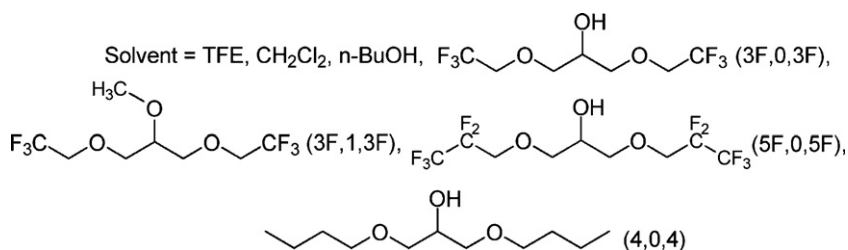
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**Scheme 1.** Glycerol derivatives solvents used to carry out the epoxidation, they have been fully described previously [47].

with aqueous hydrogen peroxide often results in extensive epoxide hydrolysis, and many efforts have been devoted to the synthesis of heterogeneous solid catalysts with hydrophobic properties [37–42]. More recently, the use of polyoxometalates and analogous systems has emerged as an interesting alternative [3,43].

Another alternative would be the use of homogeneous catalysts in a specially designed liquid phase which should be tuned in such a way that easy separation of reagents and products from the catalyst-containing phase should become more straightforward [44]. The catalytically active phase could thus be reused for more reaction cycles. Very often, recovery is accomplished by extraction with an immiscible solvent [45]. Another attractive way is to distill out reagents and products from that liquid phase which contains the catalyst. This strategy has been described for other reactions in the case of ionic liquids [46], but to the best of our knowledge it has not been applied to oxidation reactions yet.

We have recently described the synthesis and characterization of a family of glycerol-derived solvents [47]. These solvents present some new and attractive advantages, as there are made from a renewable source, they are (presumably) low toxic, exhibit a low volatility, and possess tuneable physico-chemical properties. We have previously described the use of some of these glycerol-derived solvents in the homogeneously catalyzed epoxidation reaction of cyclooctene, using aqueous hydrogen peroxide as oxidant and bis[3,5-bis(trifluoro-methyl)diphenyl] diselenide as catalyst precursor [48].

Although classically this catalytic system had been dominated by the use of dichloromethane (DCM) and 2,2,2-trifluoroethanol (TFE) as solvents [25,26], it was found that some of the glycerol-derived solvents are as good as TFE in some cases and often better than DCM. The best glycerol-based solvents in that study were those containing short fluorinated chains (see Scheme 1). The beneficial effect of trifluoroethanol as a solvent – besides being a polar, non-coordinating, non-basic and stable solvent – has been ascribed to its activating properties towards HOOH. Hydrogen peroxide becomes a better nucleophile through exceptional H-bond ability of TFE [49–52]. It can be assumed that this effect can also partially take place for some of our fluorinated glycerol-based solvents.

In this paper we explore the possibility of combining the advantages of using hydrogen peroxide, an homogeneous catalyst (namely an arylseleninic acid) [21,28,53,54], and solvents from renewable sources (glycerol-derived solvents), with tailored properties, to extend the range of applicability of these catalytic systems to the epoxidation of a more challenging substrate, such as cyclohexene, as well as to have a proof-of-principle for recyclable catalytic liquid phases with our innovative solvents (Scheme 2).

## 2. Experimental

### 2.1. Materials and equipment

#### 2.1.1. Materials

Cyclohexene (99%, Sigma–Aldrich 29240), cyclooctene, (90%, Fluka 29650), 1,2-dimethoxyethane (99.5%, Sigma–Aldrich 259527),

manganese dioxide (Sigma M3138), sodium sulfate (Scharlau SO0664) and hydrogen peroxide (Scharlab HI0139) are commercially available. Common solvents such as 2,2,2-trifluoroethanol (99%, ABCR AB102852), dichloromethane (99.9% Scharlau CL0348) and *n*-butanol (99.4%, Sigma–Aldrich 360465), are also commercially available.

Glycerol-based solvents were obtained by ring opening of either the appropriate glycidol ether (non-symmetric glycerol based solvents) or epichlorohydrin (symmetric glycerol-based solvents) with corresponding alkoxide in alcoholic media, as previously described [47], and were purified by vacuum distillation.

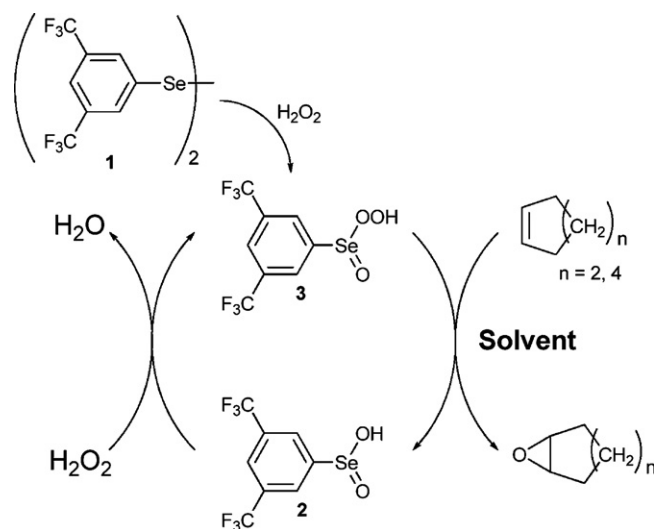
The catalyst bis[3,5-bis(trifluoro-methyl)diphenyl] diselenide was obtained as described in the literature [55].

#### 2.1.2. Equipment

Reactions were followed by gas chromatography in an Agilent 6890 apparatus equipped with an automatic injector and a FID detector. Two different experimental conditions, shown in Supplementary material, were necessary to use to analyze both olefins. Olefin conversion and olefin oxide yield were determined by area integration of gas chromatography peaks, following calibration equations carried out with ethylene glycol dimethyl ether (glyme) as an internal standard.

### 2.2. Oxidation reactions

The general procedure to the epoxidation of alkenes was carried out at 25 °C, using the following conditions: 0.8–1.0 mol% of bis[3,5-bis(trifluoro-methyl)diphenyl] diselenide was dissolved in 2 mL of solvent. Next, the hydrogen peroxide (50%) was added. When the solution became colourless, 2 mmol of ethylene glycol dimethyl



**Scheme 2.** Catalytic cycle proposed in the literature to explain the epoxidation cyclooctene and cyclohexene with arylseleninic acid–hydrogen peroxide [21,25].

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