A Selenium Catalyzed Epoxidation in Perfluorinated Solvents with Hydrogen Peroxide

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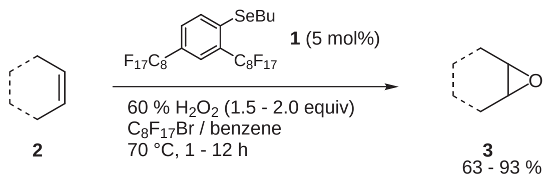
Abstract: The readily prepared 2,4-bisperfluorooctylphenyl butylselenide catalyzes the epoxidation of various olefins with hydrogen peroxide in a fluorous biphasic system. The catalyst is selectively soluble in perfluorinated solvents and can easily be recovered simply by phase separation. Furthermore, the catalyst can be reused several times without a decrease of yield and an increase of reaction time.

Key words: fluorous biphase system, catalysis, selenium, hydrogen peroxide, epoxidation

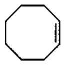
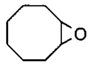
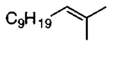
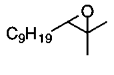
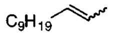
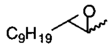
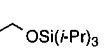
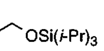
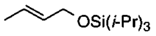
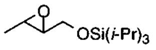
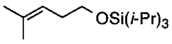
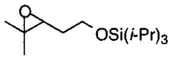
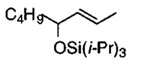
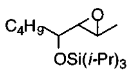
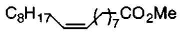
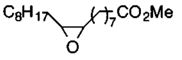
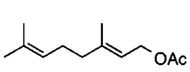
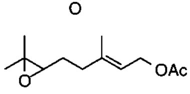
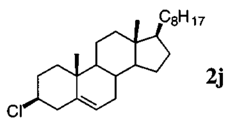
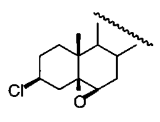
Despite the availability of numerous epoxidation conditions, there is still a need for epoxidation procedures requiring only cheap oxidation reagents like oxygen or hydrogen peroxide and readily recoverable or non-polluting oxidation catalysts. An attractive epoxidation procedure discovered by Sharpless uses phenylseleninic acid as catalyst and hydrogen peroxide or *t*-butylhydroperoxide as oxidant.[1] The toxicity of selenium compounds precludes many applications of this catalytic epoxidation. To avoid contamination of the reaction products with selenium compounds polystyrene-bound phenylseleninic acid has been used.[2] An alternative to the solid phase chemistry is the fluorous biphase catalysis[3] introduced by Horváth and Rábai.[3a] In those systems the catalyst is immobilized in the fluorous phase which ensures a facile and efficient separation of the catalyst from the reaction mixture. Recently, this method has found many applications in organic synthesis, especially in oxidation chemistry.[4] Herein, we wish to report the straightforward synthesis of a new phenylselenide **1** bearing perfluoroalkyl substituents which are necessary for selective solubilization in perfluorinated solvents. Furthermore its application in catalytic epoxidations is presented. With 5 mol% of the catalyst **1** various polysubstituted olefins **2** are oxidized in a biphasic system of benzene and bromoperfluorooctane[5] using hydrogen peroxide (60 % in water; 1.5 - 2.0 equiv) leading to epoxides **3** in good yields (Scheme 1 and Table 1). The use of 60 % hydrogen peroxide is necessary since the 30 % solution leads to emulsion of the reaction mixture.



Scheme 1

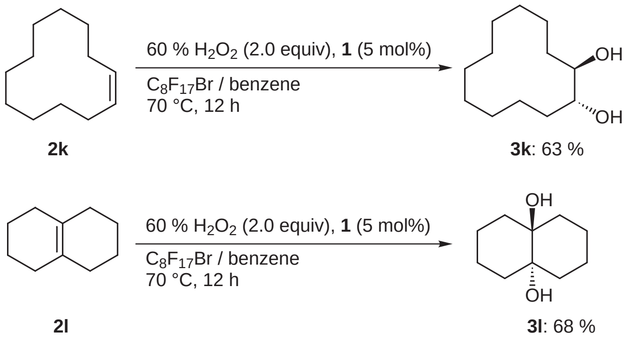
In this reaction the aryl butylselenide **1** is oxidized *in situ* by hydrogen peroxide to the corresponding arylselenic acid. We believe that this acid is oxidized to the peracid which catalyses the epoxidation of olefins as described in the literature.[1]

Table 1. Epoxides **3a-j** obtained by the oxidation of the alkenes **2a-j** in a biphasic system of benzene and bromoperfluorooctane using H_2O_2 (60 % in water) as oxidation agent.

Entry	Alkene of Type **1**	Epoxide of Type **3**	Yield (%)[a]
1	 **2a**	 **3a**	92
2	 **2b**	 **3b**	93
3	 **2c**	 **3c**	80
4	 **2d**	 **3d**	81
5	 **2e**	 **3e**	81
6	 **2f**	 **3f**	97
7	 **2g**	 **3g**	97[b]
8	 **2h**	 **3h**	84
9	 **2i**	 **3i**	63
10	 **2j**	 **3j**	80[c]

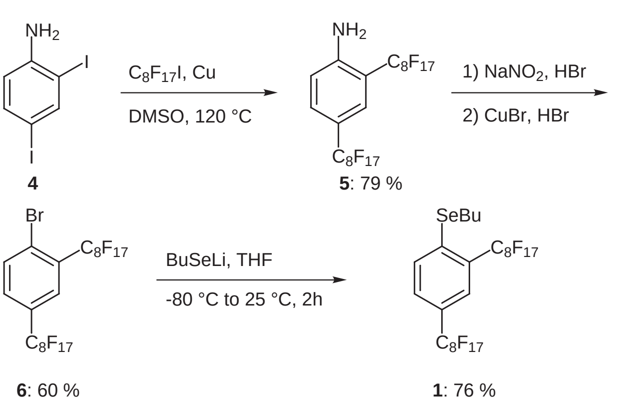
[a]Isolated yield of analytically pure product; [b]1:1 Mixture of diastereoisomers; [c]4:1 Mixture of diastereoisomers

Using 5 mol% of the selenide **1** the reactions are complete at 70 °C after 1 - 12 h. Less amounts of the catalyst lead to longer reaction time or incompletion of the reaction. The reaction tolerates the presence of an ester function (entry 8 and 9 of Table 1) as well as silyl ethers (entries 4 - 7 of Table 1). Interestingly, in the case of cyclododecene (**2k**) and octahydronaphthalene (**2l**) no formation of the epoxide was observed but instead the corresponding *trans*-diols **3k** and **3l** in respectively 63 % and 68 % yield (Scheme 2).



Scheme 2

The selenium catalyst **1** is readily prepared in three steps starting from 2,4 diiodoaniline (**4**). Ullmann-type reaction with iodoperfluorooctane in DMSO in the presence of copper powder (120 °C, 1 h) afforded the doubly perfluoroalkylated product **5** in 79 % yield.[6] Sandmeyer-reaction (i. $NaNO_2$, HBr; ii. CuBr, HBr) yielded the corresponding aryl bromide **6** in 60 % yield. After substitution with lithium butylselenide in THF at -78 °C to 25 °C the aryl butylselenide **1** was obtained in 76 % yield (Scheme 3).[7]



Scheme 3

The leaching of the catalyst was followed by ^{19}F-NMR. Thus the reaction has been carried out in the presence of fluorobenzene as internal standard under the conditions described above. After separation of the two phases the ^{19}F-NMR spectrum of the organic phase indicated that only 0.1 % of the catalyst has been moved to the benzene phase which demonstrates its excellent solubility in fluorinated solvents. The catalyst can be reused more than ten times without decrease in yield nor increase in reaction time. In the case of the epoxidation of cyclooctene (**2a**) the reaction was repeated ten times with the same catalyst solution leading to cyclooctene oxide (**3a**) in 90 - 93 % yield within 1 h. Only in the first run a longer reaction time was required because of the initial formation of the catalyst (Table 2).[8]

Table 2. Epoxidation of cyclooctene (**2a**) by reusing the catalyst **1**

Run	Yield (%)	t (h)	Run	Yield (%)	t (h)
1	92	2	6	91	1
2	91	1	7	90	1
3	92	1	8	90	1
4	90	1	9	91	1
5	93	1	10	90	1

In summary, we have described an efficient selenium catalyzed epoxidation of alkenes in a fluorous biphase system. The toxic selenium catalyst can be immobilized in perfluorinated solvents which allows the facile separation from the reaction mixture and its reuse for further reaction runs.

Other applications of the selenium catalyst in oxidation chemistry are currently investigated in our laboratory.

Acknowledgement

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References and Notes

(1) (a) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947; (b) Hori, T.; Sharpless K. B. *J. Org. Chem.* **1978**, *43*, 1689; (c) Kuwajima, I.; Shimizu, M.; Urabe, H. *J. Org. Chem.* **1982**, *47*, 837; (d) Grieco, P. A.; Yokoyama, Y.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 2034; (e) Syper, L. *Synthesis* **1989**, 167.

(2) Taylor, R. T.; Flood, L. A. *J. Org. Chem.* **1983**, *48*, 5160.

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(4) (a) Klement, I.; Lütjens, H.; Knochel, P. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1496; (b) Pozzi, G.; Banfi, S.; Manfredi, A.; Montanari, F.; Quici, S. *Tetrahedron* **1996**, *52*, 11879; (c) Pozzi, G.; Cinato, F.; Montanari, F.; Quici, S. *J. Chem. Soc. Chem. Commun.* **1998**, 877; (d) Betzemeier, B.; Lhermitte, F.; Knochel, P. *Tetrahedron Lett.* **1998**, *39*, 6667.

(5) The use of other perfluorinated solvents such as perfluorohexane and perfluorodecaline led to similar results. Benzene has been used as organic reaction medium since toluene is oxidized under the reaction conditions.

(6) Yoshino, N.; Kitamura, M.; Seto, T.; Shibata, Y. Abe, M.; Ogino, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2141.

(7) Analytical data for $C_{26}H_{12}F_{34}Se$ (**1**): ^{1}H-NMR (300 MHz, THF-d_8): δ 7.88 (d, J = 6.9 Hz, 1H), 7.74 (m, 2H), 3.13 (t, J = 7.5 Hz, 2H), 1.74 (quint, J = 6.9 Hz, 2H), 1.48 (sext, J = 7.5 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C-NMR (75 MHz, THF-d_8): δ 141.9, 133.0, 131.2 (m), 129.4 (t, J = 24.6 Hz), 128.7 (m), 127.0 (t, J = 24.8 Hz), 120.3 - 109.5 (m, 16C), 32.1, 27.9, 24.0, 13.9; MS (EI, 70 eV): 1049 (M^+, 20%); MA ($C_{26}H_{12}F_{34}Se$) calcd. C 29.76, H 1.15; Found C 29.75, H 1.39.

(8) **Typical procedure**: Preparation of cyclooctene oxide (**3a**): A 50 mL Schlenk-tube was charged with 2,4-bis(perfluorooctyl)-phenylbutylselenide (**1**) (264 mg, 0.25 mmol) dissolved in bromoperfluorooctane (5 mL) and benzene (5 mL). After addition of cyclooctene (**2a**) (550 mg, 5.0 mmol), hydrogen peroxide (60 % in H_2O, 482 mg, 8.5 mmol, 1.5 equiv). The heterogeneous reaction mixture was heated to 70 °C leading to an almost homogeneous pale yellow solution. After several minutes a decolorisation is observed due to the oxidation of the catalyst. The reaction was complete after 2 h as indicated by GC analysis of a reaction aliquot. The reaction mixture was cooled to 25 °C leading to the formation of two phases. The colorless fluorous phase was separated, washed with benzene (3 x 3 mL) and was ready for further runs. The combined benzene phase was diluted with ether (30 mL) and washed with an aqueous solution of $Na_2S_2O_5$ (20 mL) in order to destroy the excess of hydrogen peroxide, then with brine (20 mL). After drying ($MgSO_4$)and evaporation of the solvents, the resulting crude oil was purified by flash chromatography (pentane/ether 19:1) yielding pure cyclooctene oxide (**3a**, 658 mg, 92 % yield) as a colorless solid (mp: 55-56 °C).