$FeCl_3 \cdot 6H_2O$ Supported on SiO_2 Catalysed Ring Opening of Epoxides with Alcohols, Acetic Acid, Water, Chloride, Bromide and Nitrate Ions

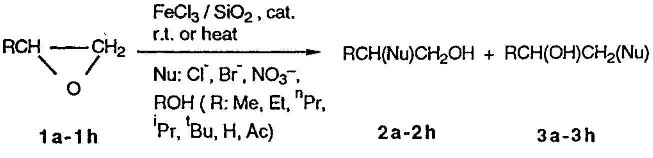
Nasser Iranpoor,* Tahere Tarrian, Zarangiz Movahedi
Chemistry Department, College of Science, Shiraz University, Shiraz 71454, Iran
Fax +98(71)20027

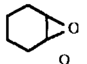
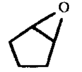
Received 6 April 1996

$FeCl_3 \cdot 6H_2O$ absorbed on chromatographic silica gel can act as an efficient catalyst for alcoholysis, hydrolysis and acetolysis of epoxides. Methanolysis of (*R*)-styrene oxide proceeds with high stereospecificity and in excellent yield. This catalyst can also convert epoxides to their corresponding β-halohydrins and β-nitrato alcohols in the presence of chloride, bromide and nitrate ions respectively.

Highly dispersed mineral solids have been used by chemists, especially in specific areas, for a considerable time. Many organic reactions have been devised in which the reagents are supported on various inorganic solids and used for variety of organic reactions.[1-4] Among metal ion supported reagents, iron has been considered with more interest due to its abundance, cheapness and especially its non-toxicity.[5] Silica-bound iron(III) chloride ($FeCl_3/SiO_2$) which can be easily prepared from dispersing $FeCl_3 \cdot 6H_2O$ onto silica gel,[6] iron(III) nitrate on bentonite A and clay-supported iron(III)[7] have been used in many organic reactions such as oxidation of organic compounds,[8,9] dehydration and rearrangement of alcohols,[6] one-electron transfer oxidative coupling of substituted aromatic compounds[8,10] and thioacetallization of aldehydes and ketones.[11]

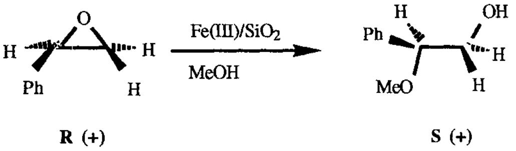
Recently, iron(III) chloride dispersed on 3Å molecular sieves has also been reported for catalytic methoxymethylation of alcohols.[12] We now report that $FeCl_3 \cdot 6H_2O/SiO_2$ can act as an efficient catalyst for the ring-opening reaction of different epoxides with various nucleophiles such as alcohols, water, acetic acid, chloride, bromide and nitrate ions (Scheme 1).



1	R	1	R or epoxide
a	Ph-	e	PhO-
b	$ClCH_2$-	f)	
c	$CH_2=CH-CH_2OCH_2$-	g)	
d	$(CH_3)_2CHOCH_2$-	h)	

Scheme 1

Iron(III) chloride absorbed on silica gel was easily prepared from a known procedure.[6] Alcoholysis and acetolysis of different classes of epoxides have been performed in different alcohols or in acetic acid in the presence of this catalyst at room temperature or under reflux conditions.[5] High yields of the corresponding β-alkoxy and acetoxy alcohols were obtained (Table 1). Room temperature hydrolysis of epoxides to the corresponding diols were also performed in the presence of this catalyst, in aqueous acetonitrile, and in good yields (Table 2). Although Lewis acids such as $BF_3 \cdot OEt_2$,[13] $SnCl_4$[13] or anhydrous $FeCl_3$[14] have been reported to act as catalysts for alcoholysis of epoxides, our observation showed that these catalysts are not reactive in the presence of nucleophiles such as halides and nitrate ions. This is due to the reaction and complex formation between these catalysts and halides and nitrate ions prior to any interaction with epoxides. However, we found that when iron(III) chloride is supported on silica gel ($FeCl_3 \cdot 6H_2O/SiO_2$), it acts as an efficient catalyst in the reaction of epoxides with chloride, bromide and nitrate ions. The reaction of these epoxides with chloride ion (as benzyl tributyl ammonium chloride) and bromide and nitrate ions (as their tetrabutyl ammonium salts) occurred in anhydrous acetonitrile and in the presence of catalytic amounts of this reagent. The corresponding β-halohydrins and β-nitrato alcohols were obtained in good to excellent yields (Table 3). The reaction of cyclic epoxides with different nucleophiles were completely anti-stereoselective and *trans* products were obtained in high yields. In the case of unsymmetrical epoxides, the high regioselectivity which was obtained in these reactions strongly depends on the nature of the substitutent on the substrate and is charge controlled. Stereospecificity of the reaction was studied by using optically active (*R*)-styrene oxide and performing the reaction in methanol. The reaction was temperature dependent and the best result was obtained in the presence of 0.1 molar equivalent of the catalyst at 0 °C. The optical rotation of the obtained 2-phenyl-2-methoxyethanol was compared with the reported data in the literature.[13] The enantiomeric purity of the product was found to be 93 %.

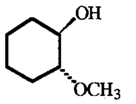
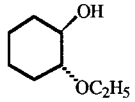
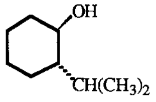
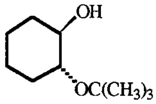
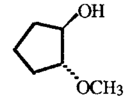
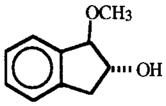


Scheme 2

The results obtained from the reaction of optically active styrene oxide with Fe(III)/SiO₂ are compared with some of those reported in the literature (Table 4).

Although the enantiomeric excess in the reactions with

Table 1. Reactions of **1a**–**1h** with Alcohols Catalyzed by Fe(III)/SiO_2

Epoxide	Solvent	Catalyst[a] / Reactant	Time (h)/ (Temp.)	Product[b]	Yield[c] (%)	bp (°C)/Torr or n_D^{25} Found	bp (°C)/Torr or n_D^{25} Reported
1a	CH_3OH	0.05	0.25 (25 °C)	**2a**	95	60/2	75/0.7[13–18]
1a	C_2H_5OH	0.05	0.75 (25 °C)	**2a**	90	1.5144	1.5143[13–15]
1a	C_3H_7OH	0.05	1.5 (25 °C)	**2a**	90	1.5109	1.5106[13–15]
1a	$(CH_3)_2CHOH$	0.05	1.5 (25 °C)	**2a**	92	1.5071	1.5075[13–15]
1a	$(CH_3)_3COH$	0.1	2 (25 °C)	**2a**	70	1.5129	1.5130[13–15]
1a	$(CH_3)_3COH$	0.15	1 (85 °C)	**2a**	85	1.5130	1.5130[13–15]
1b	CH_3OH	0.15	3.5 (25 °C)	**3b**	91	98–100/9	105/10[13–15,19]
1b	$(CH_3)_2CHOH$	0.15	2 (85 °C)	**3b**	93	107–110/10	108–110/10[13–15,19]
1b	$(CH_3)_3COH$	0.15	2.5 (85 °C)	**3b**	90	1.4432	1.4435[14]
1c	EtOH	0.2	2.5 (80 °C)	**3c**	94	1.4373	1.4375[13–15]
1c	C_3H_7OH	0.1	0.5 (100 °C)	**3c**	88	1.4383	1.4380[13–15]
1c	$(CH_3)_3COH$	0.1	1.75 (85 °C)	**3c**	85	1.4582	1.4580[13–15]
1d	CH_3OH	0.2	2 (80 °C)	**3d**	90	201–202/760	200–203/760[13,19]
1d	C_2H_5OH	0.1	1 (80 °C)	**3d**	91	209–210/760	209/760[13,20]
1d	$(CH_3)_2CHOH$	0.1	1 (85 °C)	**3d**	92	1.4199	1.4196[13,19]
1e	C_3H_7OH	0.1	1 (100 °C)	**3e**	91	1.5040	1.5042[13,21]
1e	$(CH_3)_2CHOH$	0.1	1.25 (85 °C)	**3e**	92	1.4975	1.4972[13,15]
1e	$(CH_3)_3COH$	0.2	3 (85 °C)	**3e**	89	1.4951	1.4950[13–15]
1f	CH_3OH	0.1	1.5 (25 °C)		94	100–102/60	107–111/65[13,22]
1f	C_2H_5OH	0.1	2.5 (25 °C)		90	72–73/11	80–85/15[13,22,23]
1f	$(CH_3)_2CHOH$	0.15	3.5 (25 °C)		90	80–81/16	89–93/18[13–22]
1f	$(CH_3)_3COH$	0.2	2 (85 °C)		90	90–91/15	86–91/14[13,22]
1g	CH_3OH	0.1	1.5 (25 °C)		91	174/760	175/760[13,24]
1h	CH_3OH	0.1	0.5 (25 °C)		86	146–147/11	146–148/11[13,25,26]

[a] Mole ratio of catalyst to reactant.

[b] The product was isolated and compared with authentic sample.

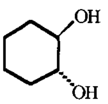
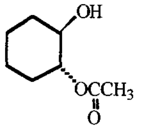
[c] Yields refer to isolated products.

$SnCl_4$ and $TiCl_4$ was high, the problem of their handling remained. In comparison, the yield of the reaction with Fe(III)/SiO_2 is higher with the advantage of ease of handling of catalyst. As was mentioned, Fe(III)/SiO_2 has been observed to act as a one-electron transfer agent in some organic reactions.[8–10] In our case, the precise mechanism of the reactions is not clear, but the possibility of the occurrence of a one-electron transfer reaction cannot be ruled out. In support of this mechanism, alcoholysis of styrene oxide in different alcohols was performed in the presence of excess acryl amide. A great decrease in the reaction rate was observed with the formation of some polyacryl amide. This observation could support the possibility of primary formation of an epoxonium radical cation in these reactions similar to that suggested in the reaction with anhydrous iron(III) chloride.[14]

In conclusion, Fe(III)/SiO_2 appears to be an efficient catalyst for ring opening of epoxides with a variety of nucleophiles under mild conditions. In addition, the advantages such as high regio- and stereoselectivity of the reactions, non-toxicity, stability and cheapness of the catayst, high yield and ease of workup make this method a useful addition to the present methodologies in organic syntheses.

Products were characterized by comparison of their physical data, IR, NMR and mass spectra with those prepared in accordance with

Table 2. Hydrolysis and Acetolysis of **1a**–**1h** Catalyzed with Fe(III)/SiO_2

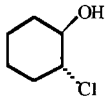
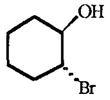
Epoxide	Solvent	Catalyst[a] / Reactant	Time (h)/ (Temp.)	Product[b]	Yield[c] (%)	bp (°C)/Torr or mp (°C)	
						Found	Reported
1a	H_2O/CH_3CN	0.2	2 (25°C)	**2a**	85	64–65	65–67[26]
1b	H_2O/CH_3CN	0.4	5 (25°C)	**3b**	80	119–120/18	115–120/18[27]
1c	H_2O/CH_3CN	0.4	5 (25°C)	**3c**	79	1.5582	1.4584[16]
1d	H_2O/CH_3CN	0.4	5 (25°C)	**3d**	89	140–143/8	150–152/9[1]
1e	H_2O/CH_3CN	0.4	5 (25°C)	**3e**	80	200/22	145–148/0.6[27]
1f	H_2O/CH_3CN	0.3	5 (25°C)		85	104–105	105[28]
1a	CH_3CO_2H	0.4	3.5 (25°C)	**2a**	90	163–165/15	163–170/15[29]
1b	CH_3CO_2H	0.3	4 (80°C)	**3b**	91	1.4760	1.4755[15]
1e	CH_3CO_2H	0.4	4 (80°C)	**3e**	85	174–5/10	175/10[30]
1f	CH_3CO_2H	0.3	4 (80°C)		78	1.5410	1.5418[15]

[a] Mole ratio of catalyst/reactant.

[b] The product was isolated and compared with authentic sample.

[c] Yield refers to isolated product.

Table 3. Reaction of **1a**–**1h** with Chloride, Bromide and Nitrate Ions Catalyzed with Fe(III)/SiO_2

Epoxide	Solvent	Catalyst[a] / Reactant	Time (h)/ (Temp.)	Product[b]	Yield[c] (%)	bp (°C)/Torr or mp (°C)	
						Found	Reported
1a	Cl^-/CH_3CN	0.4	2 (80°C)	**2a**	86	114–118/6	106–120/5[32]
1a	Br^-/CH_3CN	0.4	6 (25°C)	**2a**	85	36–37	38[33]
1b	Cl^-/CH_3CN	0.4	2.5 (80°C)	**3b**	92	174–175/760	176/760[34]
1b	Br^-/CH_3CN	0.3	12 (25°C)	**3b**	90	96–98/15	95–98/15[35]
1b	NO_3^-/CH_3CN	0.3	4 (80°C)	**3b**	54	75–76/7	75/7[36]
1c	Cl^-/CH_3CN	0.3	3.5 (80°C)	**3c**	80	103–105/25	107–108/31[37]
1c	Br^-/CH_3CN	0.3	3 (25°C)	**3c**	78	112/20	108–109/25[16]
1c	NO_3^-/CH_3CN	0.4	4 (80°C)	**3c**	51	84–86/2	85/2[36]
1d	Cl^-/CH_3CN	0.4	4 (80°C)	**4d**	80	87–88/20	180–184/760[38]
1d	Cl^-/CH_3CN	0.3	4 (25°C)	**4d**	78	188–190/760	187–189/760[17]
1e	Cl^-/CH_3CN	0.4	4 (80°C)	**3e**	96	136–137/8	112/1[37]
1e	Br^-/CH_3CN	0.5	11 (25°C)	**3e**	92	160–161/15	167–169/16[39]
1f	Cl^-/CH_3CN	0.3	3 (80°C)		78	71/7	93/26[34]
1f	Br^-/CH_3CN	0.3	8 (25°C)		77	84–86/10	88–90/7[40]

[a] Mole ratio of catalyst/reactant.

[b] The product was isolated and compared with authentic sample.

[c] Yield refers to isolated product.

literature procedures.[14–39] All yields refer to isolated products. Infrared spectra were recorded on a Perkin Elmer IR-157 G and a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Hitachi, R-2413, 60 MHz or Varian XL-100 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity determination of the substrate and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument.

Reaction of Epoxides with Alcohols; General Procedure:
$FeCl_3 \cdot 6H_2O/SiO_2$ (0.05–2 mmol) was added to a solution of epoxide (10 mmol) in the appropriate alcohol (60 mL). The mixture was stirred for the specified time and at the appropriate temperature according to Table 1. The progress of the reaction was monitored by GLC. The solvent was evaporated, Et_2O (50 mL) was added and the mixture filtered. The solid residue was washed with Et_2O (10 mL). Evaporation of the combined organic solution followed

Table 4. Comparison of Methanolysis of (*R*)-Styrene Oxide with Different Catalysts

Lewis acid	Temp. (°C)	Yield (%)	ee (%)[a]
Fe(III)/SiO_2	0	94	93
$SnCl_4$[13]	−30	88	95
$TiCl_4$[13]	−30	80	90
$AlCl_3$[b]	0	45	58
$ZnCl_2$[13]	20	0	–
$BF_3 \cdot Et_2O$[13]	−30	92	75

[a] Values are not corrected for the optical purity of starting material. Product of Aldrich, $[\alpha]_D + 33$ (neat).

[b] 0.1 Equimolar amounts of $AlCl_3$ was used under similar conditions of the reaction with Fe(III)/SiO_2.

by vacuum distillation or column chromatography on a short column of silica gel afforded the pure product in 70–95% yield.

Reaction of Epoxides in Aqueous Acetonitrile; General Procedure:
To a solution of epoxide (10 mmol) in an equal mixture of CH_3CN, H_2O (60 mL) was added $FeCl_3 \cdot 6H_2O/SiO_2$ (2–4 mmol). The mixture was stirred for the specified time at r.t. according to Table 2. The progress of the reaction mixture was monitored by TLC using CCl_4/MeOH (10/1) as eluent. The reaction mixture was filtered and evaporated. The obtained aqueous mixture was saturated with brine and extracted with Et_2O (3 × 40 mL). The combined organic solution was dried and evaporated. Vacuum distillation or column chromatography of the product on a short column of silica gel afforded the pure product in 79–89% yield.

Reaction of Epoxides with Chloride, Bromide and Nitrate Ions; General Procedure:
$FeCl_3 \cdot 6H_2O/SiO_2$ (3–4 mmol) was added to an efficiently stirred solution of epoxide (10 mmol) in anhyd CH_3CN and either (30 mmol) benzyl tributyl ammonium chloride, tetrabutyl ammonium bromide or nitrate. The obtained mixture was then stirred for the specified time and at the appropriate temperature according to Table 3. The progress of reaction was monitored by TLC and GLC. The mixture was filtered and the solid residue was washed with Et_2O. Evaporation of the organic solution followed by chromatography on a short column of silica gel afforded the corresponding product in 55–92% yield.

We would like to acknowledge the support of this work by Shiraz University Research Council and Dr. A. A. Jarahpoor for his assistance in running the mass spectra.

(1) Posner, G.H. *Angew. Chem.* **1978**, *90* 527.
(2) McKillop, A.; Young. D.W. *Synthesis* **1979**, *401*, 481.
(3) Cornelis, A.; Laszlo, P.; Pennetreau, P. *Clay Miner.* **1983**, *18*, 437; *Chem. Abstr.* **1984**, *100*, 102362.
(4) Bram, G.; D'Incan, E.; Loupy, A. *Nouv. J. Chim.* **1982**, *6*, 689.
(5) Cornelis, A.; Laszlo, P. *Synthesis* **1985**, 909.
(6) Kim, K.S.; Song, Y.H.; Lee, B.H.; Hahn, C.S. *J. Org. Chem.* **1986**, *51*, 404.
(7) Tal, D.E.; Keinan, E.; Mazur, Y. *Tetrahedron* **1981**, *37*, 4327.
(8) Jempty, T.C.; Miller, L.L.; Mazur, Y. *J. Org. chem.* **1980**, *45*, 749.
(9) Cornelis, A.; Laszlo, P. *Synthesis* **1980**, 849.
(10) Jempty, T.C.; Gogins, A.Z.; Mazur, Y. *J. Org. Chem.* **1981**, *46*, 4545.
(11) Patney, H.K. *Tetrahedron Lett.* **1991**, *32*, 2259.
(12) Patney, H.K.; *Synlett* **1992**, 567.
(13) Moberg, C.; Rakos, L.; Toottie, L. *Tetrahedron Lett.* **1992, 33**, 2191.
(14) Iranpoor, N.; Salehi. P. *Synthesis* **1994**, 1152.
(15) Chini, M.; Crotti, P.; Cardelli, C.; Macchia, F. *Synlett* **1992**, 673.
(16) Iranpoor, N.; Mohannadpour Baltork, I. *Tetrahedron Lett.* **1990**, *31*, 735.
Iranpoor, N.; Mohammadpour Baltork, I. *Synth. Commun.* **1990**, *20*, 2789.
Iranpoor, N.; Mohammadpour Baltork, I.; Shiriny, F. *Tetrahedron* **1991**, *47*, 9861.
Iranpoor, N.; Shiriny, F. *Synth. Commun.* **1994**, *24*, 1959.
Salehi, P., Ph.D thesis, Shiraz University, 1995.
(17) Kabbe, H.J. *Ann.* **1962**, *214*, 656; *Chem. Abstr.* **1963**, *58*, 1376c.
(18) Iranpoor, N.Ph.D thesis, Birmingham University, 1980.
(19) Winstein, S.; Henderson, R.B. *J. Am. Chem. Soc.* **1943**, *65*, 2197.
(20) Malinovski, M.S.; Vredenski, V.M. *Ukr. Khim. Zh.* **1957**, *23*, 626. *Chem. Abstr.* **1958**, *52*, 9959i.
(21) Isbell, A. F.; Hood, D. W. *J. Chem. Eng. Data.* **1962**, *7*, part 2, 578.
(22) Mamedov, S.; Gadzehi-Zade, F. *Zh. Obshch. Khim.* **1964**, *34*, 47. *Chem. Abstr.* **1963**, *59*, 12628g.
(23) Sonoda, N.; Tsutsumi, S. *Bull. Chem. Soc. Japan* **1965**, 38, 958.
(24) Bannard, R.A.B.; Hawkins, L.R. *Can. J. Chem.* **1961**, *39*, 1530.
(25) Mousseron, M.; Granger, R. *Compt Rend.* **1937**, *205*, 327.
(26) Treibs, W.; Schroth, W. *Ann.* **1961**, *639*, 204; *Chem. Abstr.* **1962**, *55*, 27288h.
(27) Winstein, S.; Ingraham, L.L. *J. Am. Chem. Soc.* **1955**, *77*, 1738.
(28) CRC Handbook of Chemistry and Physics, 42th Edition, 1961.
(29) Roebuck, A.; Adkins, H., *Org. Synth. Coll., III*, **1955**, 217.
(30) Detelleux, E.; Jadot, J. *Bull. Chem. Soc. Roy. Sci. Liege* **1960**, *29*, 208.
(31) Ades, D.; Fontanille, M.J. *Appl. Polym. Sci.* **1979**, *23*, 11.
(32) Eliel, E.L.; Herrmann, C.; Traxler, J.T. *J. Am. Chem. Soc.* **1956**, *78*, 1193.
(33) Cowell, A.; Stille, J.K. *J. Am. Chem. Soc.* **1980**, *102*, 4193.
(34) CRC Handbook of Chemistry and Physics, 54th edition, CRC Press, 1974.
(35) Koelsch, C.F.; Mc Elvain, S. M. *J. Am. Chem. Soc.* **1929**, *51*, 3390.
(36) Marans, N.S.; Zelinski, R.P. *J. Am. Chem. Soc.* **1950**, *72*, 5330.
(37) Swern, D.; Billen, G.N.; Knight, H.B. *J. Am. Chem. Soc.* **1949**, *71*, 1152.
(38) Ponomarev, F.G. *Zh. Obshch. Khim.* **1952**, *22*, 929.; *Chem. Abstr.* **1953**, *47*, 3794g.
(39) Pfeiffer, P.; Bauer, K. *Chem. Ber.* **1947**, *80*, 7; *Chem. Abstr.* **1947**, *41* 3098d.
(40) Naqui, S.M.; Horwitz, J.P.; Filler, R. *J. Am. Chem. Soc.* **1957**, *79*, 6283.