

Iron(III) Trifluoroacetate as an Efficient Catalyst for Solvolytic and Nonsolvolytic Nucleophilic Ring Opening of Epoxides

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Iron(III) trifluoroacetate was used as an efficient and nonhygroscopic catalyst for the alcoholysis, hydrolysis, and acetolysis of epoxides. The addition of chloride, bromide, iodide, and nitrate ions to epoxides to produce the corresponding 2-halo and 2-nitratoalkanols and also the conversion of epoxides to acetonides and thiiranes were also performed efficiently in the presence of this catalyst.

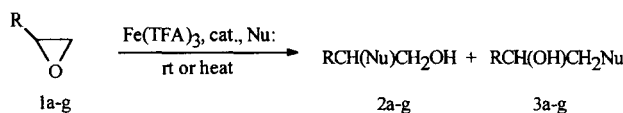
Epoxides are important intermediates in organic synthesis¹ and their reactions with different nucleophiles under both nonsolvolytic^{1–7} and solvolytic conditions have been the subject of extensive studies.^{8–14} Among solvolytic reactions of epoxides, alcoholysis has been studied in the presence of varieties of catalysts.^{8–14} Recently, we reported the use of Fe^{III} as anhydrous iron(III) chloride^{14c} or Fe^{III}/SiO₂ for alcoholysis of epoxides.^{14b} Although anhydrous iron(III) chloride has been used as an efficient catalyst for alcoholysis of epoxides, it failed to catalyze nonsolvolytic reactions of epoxides due to complex formation with anions.¹⁵ Supporting of Fe^{III} on SiO₂ removed the drawback of iron(III) chloride for the ring opening of epoxides with some nucleophiles; still, the reaction of nucleophiles such as iodide, and thiocyanate ions with epoxides did not occur in the presence of this catalyst. In addition, one of the problem encounters with supported reagents is the bulk use of the reagent and the need for excess of solvent. In this work we wish to introduce iron(III) trifluoroacetate¹⁶ as an efficient, highly stable and nonhygroscopic catalyst which can be used for both solvolytic and nonsolvolytic ring-opening reactions of epoxides with varieties of nucleophiles such as alcohols, water, acetic acid, acetone, and also chloride, bromide, iodide, nitrate, and thiocyanate ions (Scheme 1).

The alcoholysis of epoxides with primary, secondary, and tertiary alcohols was performed efficiently with this catalyst.

The results obtained from the reaction of epoxides in alcohols are given in Table 1. The regioselectivity of the reaction is controlled by electronic effects of substituents and in the case of epoxides bearing electron-withdrawing groups (1c–e), an attack of nucleophile occurs on the carbon atom away from the substituents. In the case of cyclic epoxides, the products were found to have a trans stereochemistry. In order to study the stereospecificity of this reaction, the reaction of optically active (*R*)-(+)-styrene oxide with methanol was performed in the presence of a 0.1 molar amount of the catalyst at 0 °C. The reaction was found to be highly stereospecific and (*S*)-(+)-2-methoxy-2-phenylethanol was obtained in 93% yield and 96% optical purity. The optical rotation of the product was compared with the reported data in the literature.¹⁷

Although anhydrous iron(III) chloride has only been used for the alcoholysis of epoxides, iron(III) trifluoroacetate similar to Fe^{III}/SiO₂ can also be used for the hydrolysis and acetolysis of epoxides. The results of these reactions are shown in Table 2. Catalytic quantities of the catalyst (0.1–0.3 molar amount) are required to convert epoxides to their corresponding diols or 2-acetoxyalkanols in 78–95% yields. The hydrolysis of (*R*)-(+)-styrene oxide in the presence of a 0.1 molar amount of this catalyst at 0 °C in acetonitrile/water (1 : 1) gave (*S*)-(+)-1-phenyl-1,2-ethandiol¹⁸ in 88% yield and 82% optical purity.

The use of anhydrous iron(III) chloride as a catalyst for



(a) R = Ph (b) CH₃(CH₂)₃- (c) CH₂=CHCH₂OCH₂- (d) ClCH₂- (e) PhOCH₂-
 (f) cyclohexene oxide, (g) cyclopentene oxide

Nu: ROH, HOH, AcOH, Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻

Scheme 1.

Table 1. Alcoholysis of Epoxides Catalyzed with Fe(TFA)₃

Entry	Epoxide	R'OH ^{a)}	Product ^{b)}	Time/min (Temp/°C)	Catalyst	Yield ^{c)} %
					10 ⁻² molar amount	
1	1a	A	PhCH(OCH ₃)CH ₂ OH	10 (25)	5	99
2	1a	B	PhCH(OC ₂ H ₅)CH ₂ OH	45 (25)	5	98
3	1a	C	PhCH(OC ₃ H ₇)CH ₂ OH	60 (25)	5	92
4	1a	D	PhCHOCH(CH ₃) ₂ CH ₂ OH	60 (25)	10	95
5	1a	E	PhCHOC(CH ₃) ₃ CH ₂ OH	120 (85)	15	87
6	1b ^{d)}	A	CH ₃ (CH ₂) ₃ CH(OCH ₃)CH ₂ OH	30 (25)	10	80
7	1b ^{d)}	C	CH ₃ (CH ₂) ₃ CHOCH(CH ₃) ₂ CH ₂ OH	60 (25)	15	86
8	1c	A	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ OCH ₃	60 (65)	10	85
9	1c	B	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ OC ₂ H ₅	90 (80)	10	91
10	1c	C	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ OC ₃ H ₇	75 (100)	15	94
11	1d	A	ClCH ₂ CH(OH)CH ₂ OCH ₃	120 (65)	10	92
12	1d	C	ClCH ₂ CH(OH)CH ₂ OC ₃ H ₇	75 (100)	25	86
13	1e	A	PhOCH ₂ CH(OH)CH ₂ OCH ₃	120 (65)	10	94
14	1e	B	PhOCH ₂ CH(OH)CH ₂ OC ₂ H ₅	90 (80)	10	92
15	1e	D	PhOCH ₂ CH(OH)CH ₂ OCH(CH ₃) ₂	90 (85)	15	95
16	1f	A	<i>trans</i> -2-Methoxycyclohexanol	25 (25)	5	92
17	1f	C	<i>trans</i> -2-Propoxycyclohexanol	60 (25)	5	90
18	1f	D	<i>trans</i> -2-Isopropoxycyclohexanol	60 (25)	10	96
19	1f	E	<i>trans</i> -2-Tertiarybutoxycyclohexanol	75 (25)	15	83
20	1g	A	<i>trans</i> -2-Methoxycyclopentanol	45 (25)	5	90
21	1g	B	<i>trans</i> -2-Ethoxycyclopentanol	60 (25)	5	92
22	1g	D	<i>trans</i> -2-Isopropoxycyclopentanol	60 (25)	10	90
23	1g	E	<i>trans</i> -2-Tertiarybutoxycyclopentanol	75 (25)	15	80

a) A: Methanol, B: Ethanol, C: 1-Propanol, D: 2-Propanol, E: *t*-Butanol. b) All the products are known compounds and were identified by comparison with known samples. c) Isolated yield. d) Formation of 10–15% of the minor isomer from attack of alcohol to the primary carbon of epoxide ring was also observed by GC and NMR analysis.

Table 2. Hydrolysis and Acetolysis of Epoxides Catalyzed with Fe(TFA)₃

Entry	Epoxide	Solvent ^{a)}	Product ^{b)}	Time/min (Temp/°C)	Catalyst	Yield ^{c)} %
					10 ⁻² molar amount	
1	1a	A	PhCH(OAc)CH ₂ OH	45 (25)	10	95
2	1a	B	PhCH(OH)CH ₂ OH	10 (25)	10	85
3	1b ^{d)}	A	CH ₃ (CH ₂) ₃ CH(OAc)CH ₂ OH	30 (25)	10	80
4	1b	B	CH ₃ (CH ₂) ₃ CH(OH)CH ₂ OH	50 (25)	10	91
5	1c	A	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ OAc	180 (100)	15	82
6	1c	B	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ OH	180 (80)	10	80
7	1d	A	ClCH ₂ CH(OH)CH ₂ OAc	120 (100)	15	90
8	1d	B	ClCH ₂ CH(OH)CH ₂ OH	240 (80)	15	87
9	1e	A	PhOCH ₂ CH(OH)CH ₂ OAc	120 (100)	20	83
10	1e	B	PhOCH ₂ CH(OH)CH ₂ OH	90 (80)	20	82
11	1f	A	<i>trans</i> -2-Acetoxycyclohexanol	15 (25)	10	89
12	1f	B	<i>trans</i> -1,2-Cyclohexanediol	20 (25)	10	83
13	1g	A	<i>trans</i> -2-Acetoxycyclopentanol	25 (25)	10	87
14	1g	B	<i>trans</i> -1,2-Cyclopentanediol	45 (25)	15	80

a) A: Acetic acid, B: Aqueous acetonitrile. b) All the products are known compounds and were identified by comparison with known samples. c) Isolated yield. d) GC and NMR analysis of the crude reaction mixture showed the formation of 14% of the other isomer.

nonsolvolytic ring opening of epoxides with anions including halides has not been successful.¹⁵ However, we were able to use Fe^{III}/SiO₂ as a catalyst for the conversion of epoxides to 2-chloro- and 2-bromoalkanols. The reaction of epoxides with iodide ion in the presence of Fe^{III}/SiO₂ was not successful due to the oxidation of iodide ion to iodine with a subsequent formation of I₃⁻. By using iron(III) trifluoroacetate as a

catalyst, we were able to do ring opening of epoxides with chloride, bromide, and iodide in high-to-excellent yields in dry acetonitrile. The reactions proceed very well with the quaternary ammonium halides as well as with their ammonium salts. The reactions of epoxides with ammonium iodide were found to be very efficient and only 0.05 molar amount of the catalyst was required to give the corresponding 2-

Table 3. Conversion of Epoxides to 2-Halo- and 2-Nitratoalkanols Catalyzed with Fe(TFA)₃

Entry	Epoxide	Reagent	Product ^{a,b)}	Time/min (Temp/ ^o C)	Catalyst		Yield ^{c)} %
					10 ⁻²	molar amount	
1	1a	Bu ₃ BnNCl	PhCH(Cl)CH ₂ OH	6 (25)	10		90
2	1a	NH ₄ Cl	PhCH(Cl)CH ₂ OH	5 (25)	20		85
3	1a	Bu ₄ NBr	PhCH(Br)CH ₂ OH	2 (25)	10		92
4	1a	NH ₄ Br	PhCH(Br)CH ₂ OH	2 (25)	15		85
5	1a	Bu ₄ NI	PhCH(I)CH ₂ OH	6 (25)	20		90
6	1a	NH ₄ I	PhCH(I)CH ₂ OH	3 (25)	5		92
7	1a	NH ₄ NO ₃	PhCH(ONO ₂)CH ₂ OH	4 (80)	30		85
8	1b	Bu ₃ BnNCl	CH ₃ (CH ₂) ₃ CH(OH)CH ₂ Cl	1 (80)	20		88
9	1b	NH ₄ Cl	CH ₃ (CH ₂) ₃ CH(OH)CH ₂ Cl	2 (80)	30		91
10	1b	Bu ₄ NBr	CH ₃ (CH ₂) ₃ CH(OH)CH ₂ Br	2 (25)	2		92
11	1b	NH ₄ Br	CH ₃ (CH ₂) ₃ CH(OH)CH ₂ Br	3 (25)	20		91
12	1b	NH ₄ I	CH ₃ (CH ₂) ₃ CH(OH)CH ₂ I	3 (25)	5		88
13	1c	NH ₄ Cl	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ Cl	2.5 (80)	30		82
14	1c	Bu ₃ BnNCl	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ Cl	2.5 (80)	30		80
15	1c	Bu ₄ NBr	CH ₂ =CHCH ₂ OCH ₂ CH(OH)CH ₂ Br	3 (80)	30		92
16	1c	NH ₄ Br	CH ₂ =CHCH ₂ OCH(OH)CH ₂ Br	4 (80)	30		94
17	1c	NH ₄ I	CH ₂ =CHCH ₂ OCH(OH)CH ₂ I	4 (80)	5		94
18	1d	NH ₄ Cl	ClCH ₂ CH(OH)CH ₂ Cl	2.5 (80)	30		93
19	1d	Bu ₄ NBr	ClCH ₂ CH(OH)CH ₂ Br	4 (80)	30		96
20	1d	NH ₄ Br	ClCH ₂ CH(OH)CH ₂ Br	5 (80)	30		93
21	1d	NH ₄ I	ClCH ₂ CH(OH)CH ₂ I	4 (25)	5		92
22	1d	NH ₄ NO ₃	ClCH ₂ CH(OH)CH ₂ ONO ₂	5 (80)	30		80
23	1e	NH ₄ Cl	PhOCH ₂ CH(OH)CH ₂ Cl	1.5 (80)	3		83
24	1e	Bu ₄ NBr	PhOCH ₂ CH(OH)CH ₂ Br	4 (80)	30		83
25	1e	NH ₄ I	PhOCH ₂ CH(OH)CH ₂ I	2 (25)	5		95
26	1e	NH ₄ NO ₃	PhOCH ₂ CH(OH)CH ₂ ONO ₂	4.5 (80)	3		90
27	1f	Bu ₃ BzNCl	<i>trans</i> -2-Chlorocyclohexanol	7 (25)	15		87
28	1f	NH ₄ Cl	<i>trans</i> -2-Chlorocyclohexanol	2 (80)	2		92
29	1f	Bu ₄ NBr	<i>trans</i> -2-Bromocyclohexanol	2 (25)	15		90
30	1f	NH ₄ Br	<i>trans</i> -2-Bromocyclohexanol	2.5 (25)	15		91
31	1f	NH ₄ I	<i>trans</i> -2-Iodocyclohexanol	3 (25)	5		96
32	1f	NH ₄ NO ₃	<i>trans</i> -2-Nitratocyclohexanol	4 (80)	30		87

a) Products were identified by comparison with known samples. b) In the reactions of 1b with halides, GC analysis of the reaction mixture showed the formation of minor isomer in 8—15% yields. c) Isolated yield.

iodoalkanols in 92—96% yields at room temperature. The results of the formation of haloalkanols are given in Table 3.

The possibility of using this catalyst for the ring opening of epoxides with NO₃⁻ was also studied. The reactions were performed in acetonitrile–water (6 : 1) under reflux conditions to give the corresponding 2-nitratoalkanols in 80—90% yields. The results are given in Table 3.

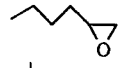
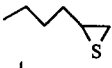
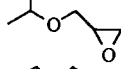
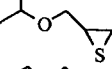
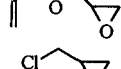
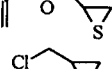
Conversion of epoxides to thiiranes with NH₄SCN and in the presence of a suitable catalyst¹⁹ under nonaqueous conditions different from classical methods which are generally carried out in homogeneous or heterogeneous aqueous media is important in organic synthesis. The reaction of epoxides with ammonium thiocyanate in the presence of 0.2 molar amounts of this catalyst was found to occur efficiently in acetonitrile at room temperature along with the formation of the corresponding thiiranes in excellent yields (91—100%). In order to show the efficiency of Fe(TFA)₃ for this transformation, the reaction of styrene oxide and thiocyanate ion in the presence of Lewis acids such as halides of Al^{III}, Sn^{II}, Mn^{II}, Zn^{II}, Fe^{II}, Fe^{III}, Co^{II}, Cu^{II}, and Ti^{IV} were studied, but all of these catalysts failed to complete the reaction possibly

due to the complex formation between SCN⁻ and the Lewis acid. Our results for this transformation are given in Table 4.

1,3-Dioxolanes are widely used protecting groups for diols²⁰ with special interest in carbohydrates and steroid chemistry. In addition, they are very suitable derivatives of diols for GC, GLC, and mass spectrometry.²¹ The direct conversion of an epoxide to 1,3-dioxolane instead of adding water to form diol with subsequent elimination in the presence of acetone has been studied with only a few reagents.²² Due to the importance of the direct synthesis of acetonides from epoxides and acetone, the ring-opening reaction of epoxides with acetone was also studied in the presence of this catalyst under reflux conditions. The results are shown in Table 5. In conclusion, iron(III) trifluoroacetate which is a stable and nonhygroscopic Fe^{III} compound, can be considered as a bench-top reagent for efficient and catalytic ring-opening reactions of epoxides with different nucleophiles under both solvolytic and nonsolvolytic reaction conditions. In addition, in the presence of this catalyst, efficient conversion of epoxides to their corresponding thiiranes and acetonides is also possible.

Experimental

Table 4. Conversion of Epoxides to Thiiranes^{a)} with Ammonium Thiocyanate Catalyzed with 0.2 Molar Amounts of $\text{Fe}(\text{TFA})_3$ at Room Temperature

Epoxide	Time/min	Yield/% ^{b)}	Product
	30	96	
	40	93	
	40	91	
	60	92	
	50	95	
	45	98	
	50	91	

a) Products were identified by comparison with known samples.

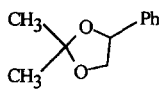
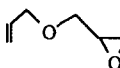
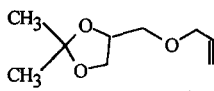
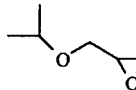
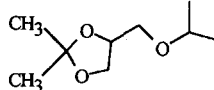
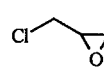
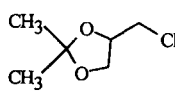
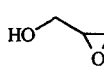
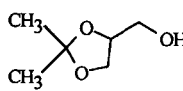
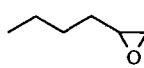
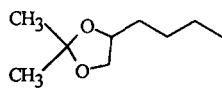
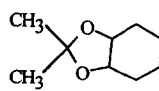
b) Isolated yield.

Products were characterized by comparisons of their physical data with those of known samples. All yields refer to isolated products. IR spectra were recorded on a Perkin–Elmer 781 and Pye Unicam 8725 spectrometers. NMR spectra were recorded on a Bruker DPX 250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000EX. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument.

Preparation of Iron(III) Trifluoroacetate. An excess of trifluoroacetic acid (5 ml) was added to anhydrous iron(III) chloride (1 g, 6.15 mmol) in a round-bottomed flask under an argon atmosphere and the resulting mixture was stirred magnetically and refluxed for 48 h. During the reaction, hydrogen chloride gas was evolved. The remaining acid was removed under reduced pressure and the residue was washed with *n*-hexane and filtered. The resulting red cake was collected and dried at 70 °C for 3 h. Iron(III) trifluoroacetate was obtained as a red color, nonhygroscopic, and stable powder in 2.39 g, 98% yield, mp 107–110 °C (lit.¹⁶ mp 108–111 °C). The reagent can be stored for extended periods of time in a closed bottle without changing.

Typical Experiments Catalyzed with Iron(III) Trifluoroacetate: Methanolysis of Styrene Oxide. To a solution of styrene oxide (120 mg, 1 mmol) in methanol (3 ml), 0.05 mmol of $\text{Fe}(\text{TFA})_3$ was added. The reaction mixture was stirred at room temperature for 10 min. The progress of reaction was monitored by GC or TLC, using hexane/EtOAc (6:1) as eluent. The solvent

Table 5. Formation of Acetonides from Epoxides in Refluxing Acetone in the Presence of $\text{Fe}(\text{TFA})_3$

Entry	Epoxide	Reaction time/h	Yield ^{a)} %	Catalyst molar amount	Product ^{b)}
1		2	85	0.1	
2		3	90	0.2	
3		3	92	0.2	
4		5	86	0.2	
5		4	89	0.2	
6		3	90	0.1	
7		2	88	0.15	

a) Yield refers to isolated product. b) The products were identified by comparison with known samples.

was evaporated and water (20 ml) was added and extracted with diethyl ether (3×20 ml). The organic layer was separated and dried with anhydrous Na₂SO₄. Evaporation of the solvent followed by chromatography on a short column of silica gel, using hexane/CCl₄ (1:1), gave 2-methoxy-2-phenylethanol as a colorless liquid in 87–99% yield, bp 65 °C/0.3 mmHg (Lit,^{14f} 75 °C/0.7 mmHg), (1 mmHg = 133.322 Pa).

Hydrolysis of Cyclohexene Oxide. A solution of epoxide (1 mmol) in a mixture of water–acetonitrile (1:1, 5 ml) was treated with 0.1 mmol of Fe(TFA)₃ at room temperature for 20 min. The progress of reaction was monitored by TLC using Hexane/EtOAc (4:1) as an eluent. The reaction mixture was saturated with sodium chloride and the product was extracted with ether several times. The organic solution was dried with anhydrous Na₂SO₄ and evaporated. Recrystallization from ethyl acetate gave *trans*-1,2-cyclohexanediol in 83% yield, mp 104–105 °C (Lit,^{14f} 105 °C).

Acetolysis of Styrene Oxide. To a solution of styrene oxide (1.2 g, 10 mmol) in acetic acid (40 ml), 1 mmol of anhydrous Fe(TFA)₃ was added and stirred at room temperature for 45 min. The progress of reaction was followed by GLC. The solvent was evaporated and water (50 ml) was added; the product was extracted with ether (3×50 ml). The etherate solution was washed with a 5% solution of sodium hydrogen carbonate and then with water and dried over anhydrous Na₂SO₄. Evaporation of the solvent followed by column chromatography on a short column of silica gel gave 2-acetoxy-2-phenylethanol as a colorless liquid in 95% yield, bp 165 °C/15 mmHg (Lit,^{14f} 163–170 °C/15 mmHg).

Reaction of Styrene Oxide with Ammonium Chloride. A mixture of Fe(TFA)₃ (0.2 mmol), styrene oxide (120 mg, 1 mmol), and ammonium chloride (3 mmol) in dry acetonitrile (5 ml) was stirred under reflux condition for 3 h. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the solid residue was washed by the solvent several times. The solvent was evaporated and water was added (15 ml); the product was extracted with ether (3×20 ml) and dried (Na₂SO₄). Evaporation of the solvent, followed by chromatography on a short column of silica gel, afforded 2-chloro-2-phenylethanol in 90% yield, bp 110–114 °C/5 mmHg (Lit,^{14f} 106–120 °C/5 mmHg).

Reaction of Cyclohexene Oxide with Tetrabutylammonium Bromide. Fe(TFA)₃ (0.75 mmol) was added to a solution of epoxide (5 mmol) and tetrabutylammonium bromide (15 mmol) in dry acetonitrile (30 ml). The mixture was stirred for 2 h at room temperature. The progress of the reaction was followed by TLC using CCl₄/ether: (8/1) as an eluent. After completion of the reaction, the mixture was filtered and the solid residue was washed with the solvent several times. After evaporation of the solvent, water (50 ml) was added and the product was extracted with ether (3×50 ml). The organic solution was dried with anhydrous Na₂SO₄. Evaporation of the solvent followed by column chromatography or distillation in vacuum afforded the *trans*-2 bromocyclohexanol in 90% yield, bp 84–87 °C/7 mmHg (Lit,^{14f} 88–90/7 mmHg).

Reaction of Cyclohexene Oxide with Ammonium Iodide. Fe(TFA)₃ (0.05 mmol) was added to a solution of cyclohexene oxide (1 mmol) and ammonium iodide (3 mmol) in acetonitrile (3 ml). The reaction mixture was stirred for 3 h at room temperature. The progress of reaction was monitored by TLC using CCl₄/ether: (6/1) as an eluent. After evaporation of the solvent, water (15 ml) was added and the product was extracted with ether (3×20 ml), and dried with anhydrous Na₂SO₄. Evaporation of solvent followed by column chromatography on silica gel gave *trans*-2-iodocyclohexanol in 96% yield. ¹H NMR (CDCl₃, 250 MHz) δ = 1.2–1.4 (3H, m), 1.8–2.0 (3H, m), 2.2–2.3 (1H, m), 2.3–2.4 (1H, m), 2.7

(1H, s), 3.6–3.65 (1H, m), 3.8–3.9 (1H, m). ¹³C NMR (CDCl₃) δ = 24.5, 26.6, 32.7, 35.5, 59.8, 71.6.

Reaction of (Chloromethyl) Oxirane with Ammonium Nitrate. To a solution of (Chloromethyl) Oxirane (10 mmol) and ammonium nitrate (30 mmol) in acetonitrile–water (40 ml: 6/1), Fe(TFA)₃ (3 mmol) was added. The mixture was refluxed for 5 h. The solvent was evaporated and to the residue was added water (50 ml). The product was extracted with ether (3×60 ml). The etherate solution was dried with anhydrous Na₂SO₄ and evaporated. The product was purified by vacuum distillation. A pure product was obtained in 80% yield, bp 78–90 °C/8 mmHg (Lit,^{14f} bp 75 °C/7 mmHg).

Conversion of Styrene Oxide to Styrene Sulfide with Ammonium Thiocyanate. To a mixture of styrene oxide (10 mmol) and ammonium thiocyanate (30 mmol) in acetonitrile (30 ml) was added Fe(TFA)₃ (2 mmol); the mixture was stirred at room temperature for 45 min. The progress of reaction was monitored by GLC. After completion of the reaction, the solvent was evaporated and CCl₄ (2×25 ml) was added to the solid residue and filtered. The filtrates were combined and concentrated under vacuum. The remaining crude product could be purified by chromatography on a short silica gel column or vacuum distillation. Pure styrene sulfide was obtained in 96% yield, bp 85–86 °C/5 mmHg (Lit,²³ bp 87–88 °C/4 mmHg).

Conversion of Styrene Oxide to 2,2-Dimethyl-4-phenyl-1,3-dioxolane in Acetone. To a solution of styrene oxide (1 mmol) in dry acetone (3 ml), Fe(TFA)₃ (0.1 mmol) was added, and refluxed for 3 h. The reaction was monitored by GLC. The solvent was evaporated and the product was chromatographed on a short column of silica gel using CCl₄/hexane (1:1) as an eluent. The product was obtained as colorless liquid in 85% yield.

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