A Novel Epoxidation Reaction of Olefins Using a Combination of Chloramine-M, Benzaldehyde, and Benzyltriethylammonium Chloride

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Abstract: A combination of Chloramine-M (CH_3SO_2NClNa), benzaldehyde, and benzyltriethylammonium chloride (BTEAC) was found to epoxidize a wide range of olefins. While epoxidation of *trans*-olefins provided exclusively *trans*-epoxides, *cis*-olefins (*cis*-stilbene, *cis*-*β*-methylstyrene, and 4-*cis*-octene) gave *trans*-epoxides as major products. Good to excellent diastereoselectivities were obtained for epoxidation of two substituted cyclohexenes. Chloramine-T was found to give a slower reaction than Chloramine-M. *cis*-*N*-Sulfonyloxaziridine **D** is proposed to be the epoxidizing agent in this novel epoxidation reaction on the basis of the mechanistic studies.

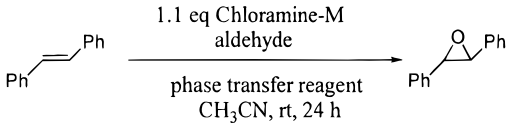
Introduction

N-Sulfonyloxaziridines have been extensively studied by Davis and co-workers as synthetically useful oxidants[1] which are highly chemoselective. For instance, they oxidize sulfides to sulfoxides without over-oxidation to sulfones. Since they are neutral aprotic oxidizing reagents, *N*-sulfonyloxaziridines are among the few reagents readily available for the oxidation of carbanions and enolates. The optically active *N*-sulfonyloxaziridines have also been developed for asymmetric oxidation of nucleophilic substrates.[2] However, the *N*-sulfonyloxaziridines employed thus far need to be prepared prior to use, mainly via oxidation of *N*-sulfonimines. On the basis of our work in oxidation chemistry using in situ generated dioxiranes,[3] which are structurally similar to oxaziridines, we developed a novel method for olefin epoxidation that employs a *cis*-*N*-sulfonyloxaziridine generated in situ from the combination of Chloramine-M,[4] benzaldehyde, and benzyltriethylammonium chloride (BTEAC).

Results and Discussion

I. A New Epoxidation System. *trans*-Stilbene was initially treated with 1.1 equiv of Chloramine-M and 1 equiv of benzaldehyde in CH_3CN at room temperature. It was encouraging to observe the formation of *trans*-stilbene oxide, though the reaction was slow. After 24 h the isolated yield of *trans*-stilbene oxide was 23% (Table 1, entry 1). However, in the presence of 18-crown-6, the isolated yield of the epoxide increased to 34% (entry 2). Replacing 18-crown-6 with BTEAC led to a 49% isolated yield of the epoxide (entry 3). Increasing the amount of benzaldehyde from 1 to 4 equiv resulted in complete reaction in 17 h at room temperature, but further increase up to 6 equiv had no significant effect (entries 3−6). 4-Methoxybenzaldehyde gave a reaction rate similar to that of benzaldehyde but a lower yield of the epoxide (entry 3 vs 7). 4-Cyanobenzaldehyde and some aliphatic aldehydes including propanal, *tert*-butanal, and isopropanal were tested, but very low reaction rates were observed. The use of other organic solvents such as CH_2Cl_2, EtOAc, DMF, THF, and DME also gave very slow reactions. Therefore, 1.1 equiv of Chloramine-M, 4 equiv of benzaldehyde, and 1 equiv of BTEAC were found to be the optimal system for this reaction (Scheme 1).

Table 1. Epoxidation of *trans*-Stilbene[a]



entry	aldehyde[b]	phase transfer reagent[c]	convn	yield (%)[d]
1	PhCHO (1)		36	23 (63)
2	PhCHO (1)	18-crown-6	57	34 (59)
3	PhCHO (1)	BTEAC	79	49 (62)
4	PhCHO (2)	BTEAC	87	51 (59)
5[e]	PhCHO (4)	BTEAC	100	63
6[f]	PhCHO (6)	BTEAC	100	65
7	*p*-MeOPhCHO (1)	BTEAC	73	24 (33)

[a] The reaction was carried out with 0.1 mmol of *trans*-stilbene. [b] The number in parentheses represents molar equivalents of aldehyde. [c] 1 equiv. [d] Isolated yield. The number in parentheses represents the yield based on recovered *trans*-stilbene. [e] The reaction time was 17 h. [f] The reaction time was 16 h.

A. Substrates. A variety of olefins (**1**−**15**) including 1,2-disubstituted olefins and trisubstituted olefins and an allylic alcohol were examined using the new epoxidation method (Chart

(1) For excellent reviews on oxaziridines, see: (a) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703−5742. (b) Davis, F. A.; Reddy, R. T. In *Comprehensive Heterocyclic Chemistry II*, 1st ed.; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Series Eds.; Pergamon: New York, 1996; Vol. 1A, Padwa, A., Ed.; pp 365−413.

(2) (a) Davis, F. A.; Chen, B.-C. *Chem. Rev.* **1992**, *92*, 919−934. (b) Davis, F. A.; Reddy, R. T.; Han, W.; Reddy, R. E. *Pure Appl. Chem.* **1993**, *65*, 633−640. (c) Davis, F. A.; Reddy, R. E.; Kasu, P. V. N.; Portonovo, P. S.; Carroll, P. J. *J. Org. Chem.* **1997**, *62*, 3625−3630. (d) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123−3126. (e) Davis, F. A.; Chattopadhyay, S. *Tetrahedron Lett.* **1986**, *27*, 5079−5082.

(3) For recent examples of epoxidation using dioxiranes generated in situ, see: (a) Yang, D.; Wong, M.-K.; Yip, Y.-C. *J. Org. Chem.* **1995**, *60*, 3887−3889. (b) Yang, D.; Yip, Y.-C.; Tang, M.-W.; Wong, M.-K.; Cheung, K.-K. *J. Org. Chem.* **1998**, *63*, 9888−9894. (c) Yang, D.; Yip, Y.-C.; Jiao, G.-S.; Wong, M.-K. *J. Org. Chem.* **1998**, *63*, 8952−8956. (d) Frohn, M.; Wang, Z.-X.; Shi, Y. *J. Org. Chem.* **1998**, *63*, 6425−6426. (e) Denmark, S. E.; Forbes, D. C.; Hays, D. S.; DePue, J. S.; Wilde, R. G. *J. Org. Chem.* **1995**, *60*, 1391−1407.

(4) For the preparation of Chloramine-M, see: Rudolph, J.; Sennhenn, P. C.; Vlaar, C. P.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2810−2813.

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Scheme 1

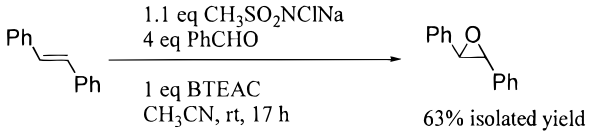


Chart 1

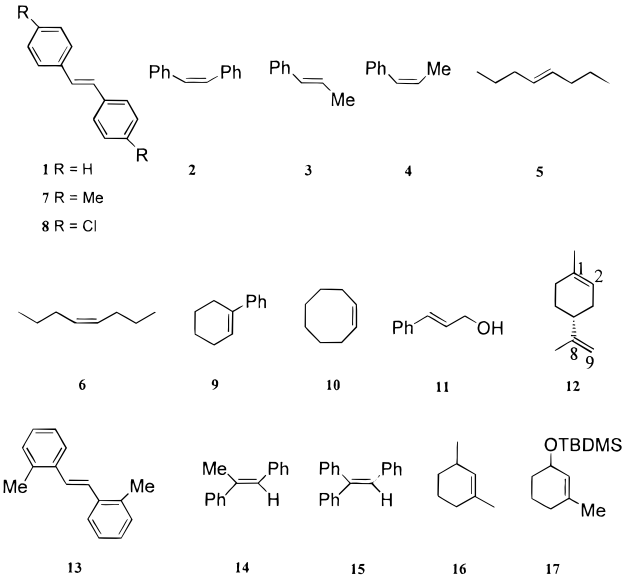


Table 2. Epoxidation of Olefins by Chloramine-M/Benzaldehyde/BTEAC[a]

entry	olefin	time (h)	epoxide yield (%)	convn of olefin (%)
1	**1**	17	63[b]	100
2	**2**	47	51 (*trans*/*cis* = 15/1)[c]	85
3	**3**	48	67[b,d]	53[d]
4	**4**	48	63[d] (*trans*/*cis* = 9/1)[c]	31[d]
5[e]	**5**	72	79[b,d]	57[d]
6[e]	**6**	72	82[d] (*trans*/*cis* = 3.4/1)[c]	42[d]
7	**7**	7	58	100
8	**8**	26	65	64
9	**9**	48	61	74
10[e]	**10**	140	71[d]	52[d]
11	**11**	65	52[f]	53
12[g]	**12**	120	76[d,h]	55[d]
13	**13**	29	66	100
14	**14**	27	59	100
15	**15**	46	73	100

[a] Unless otherwise indicated, the reaction was carried out with 0.1 mmol of olefin, 0.11 mmol of Chloramine-M, 0.4 mmol of benzaldehyde, and 0.1 mmol of BTEAC in 2 mL of anhydrous acetonitrile at room temperature. [b] *trans*-Epoxide only. [c] The ratios were obtained by GC analyses. [d] The values of conversion (%) and yield (%) were obtained by GC analyses. [e] 0.2 mmol of olefin. [f] The other product was *trans*-cinnamaldehyde (14%). [g] 1 mmol of olefin. [h] The ratio of 1,2-epoxide to 8,9-epoxide was 2.6:1 by ^{1}H NMR, and the ratio of *cis*-1,2-epoxide to *trans*-1,2-epoxide was 1.9:1 by GC or 2.0:1 by ^{1}H NMR.

1, Table 2). We found that epoxidation of *trans*-olefins gave exclusively *trans*-epoxides while *cis*-olefins gave *trans*-epoxides as the major products (entries 1−6). The nonstereospecificity of the epoxidation reaction implies that the reaction might proceed stepwise, in contrast to the stereospecific epoxidation reactions mediated by peracids and dioxiranes.[5]

We also found that electron-rich olefins gave faster epoxidation, suggesting the reaction is electrophilic in nature. *p*-Me-substituted *trans*-stilbene **7** gave faster epoxidation than **1**, whereas *p*-Cl-substituted *trans*-stilbene **8** showed a slower rate (entries 7 and 8 vs 1). Compared with **3**, the presence of the allylic hydroxyl group dramatically decreased the electron density of the double bond in olefin **11** due to the inductive effect, resulting in a slower reaction (entry 11 vs 3). In the case of (+)-limonene (entry 12), the sterically hindered trisubstituted 1,2-double bond is preferentially epoxidized due to its relatively higher electron density than that of the terminal 8,9-double bond.[6] However, substrates **2** and **13**−**15** reacted slower than *trans*-stilbene. This is partly because the electron densities of the olefin double bonds are reduced as the phenyl rings of these substrates are twisted out of the olefin plane in order to avoid steric hindrance.

Table 3. Epoxidation of Olefins by Chloramine-T/Benzaldehyde/BTEAC[a]

entry	olefin	time (h)	epoxide yield (%)	convn of olefin (%)
1	**1**	57	57	100
2	**2**	69	55 (*trans*/*cis* = 17/1)[b]	47
3[c]	**4**	69	73 (*trans*/*cis* = 10/1)[b]	10
4[c]	**6**	96	81 (*trans*/*cis* = 4/1)[b]	43

[a] Unless otherwise indicated, the reaction was carried out with 0.1 mmol of olefin, 0.11 mmol of Chloramine-T, 0.4 mmol of benzaldehyde, and 0.1 mmol of BTEAC in 2 mL of anhydrous acetonitrile at room temperature. [b] The ratio of *trans*-epoxide to *cis*-epoxide was determined by GC analyses. [c] 0.2 mmol of olefin.

Table 4. Diastereoselective Epoxidation Using Chloramine-M/Benzaldehyde/BTEAC[a]

entry	olefins	time (h)	conversion (%)	yield (%)	epoxides	*trans*/*cis* ratio[b]
1	**16**	61	61	79	*trans*- + *cis*-	4.3:1 (1.2:1)
2[c]	**17**	55	36	78	*trans*- + *cis*-	19.4:1 (7.5:1)

[a] The reaction was carried out with 0.3 mmol of olefin, 0.33 mmol of Chloramine-M, 1.2 mmol of benzaldehyde, and 0.3 mmol of BTEAC in 6 mL of anhydrous acetonitrile at room temperature. All the experimental data were obtained by GC analyses. [b] The number in parentheses represents the ratio of *trans*-epoxide to *cis*-epoxide obtained from the epoxidation with *m*-CPBA. [c] 0.1 mmol of olefin.

B. Use of Chloramine-T. Chloramine-T is an analogue of Chloramine-M and its hydrate form is commercially available.[7] Results for epoxidation of some selected olefins using Chloramine-T/benzaldehyde/BTEAC are summarized in Table 3. Though Chloramine-T had lower reactivity than Chloramine-M, epoxidation of *cis*-olefins **2**, **4**, and **6** using Chloramine-T yielded the corresponding *trans*-epoxides as the major products, similar to the case of Chloramine-M.

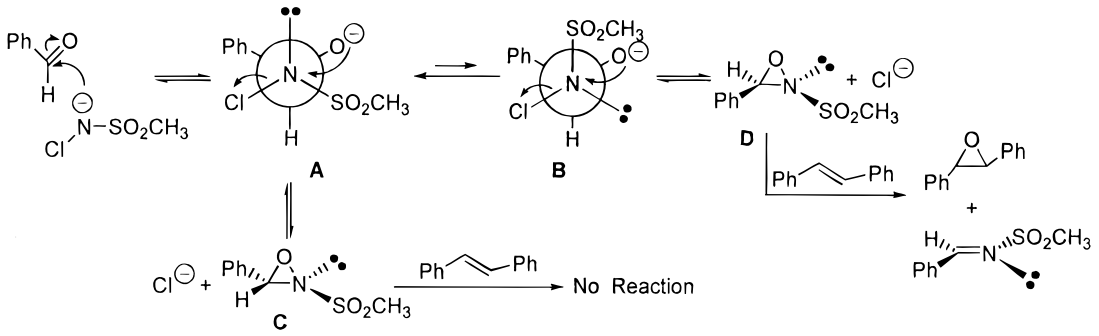
C. Diastereoselectivity Study. For substrates 1,3-dimethylcyclohexene **16** and *tert*-butyldimethyl[(3-methyl-2-cyclohexen-1-yl)oxy]silane **17**, higher *trans* to *cis* epoxide ratios were obtained using our in situ system compared with *m*-CPBA epoxidation (Table 4). Most notably, the diastereoselectivity

(5) (a) Bartlett, P. D. *Rec. Chem. Prog.* **1957**, *18*, 111. (b) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187−1201. (c) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205−211.

(6) Davis, F. A.; Towson, J. C.; Vashi, D. B.; ThimmaReddy, R.; McCauley, J. P.; Harakal, M. E. Jr.; Gosciniak, D. J. *J. Org. Chem.* **1990**, *55*, 1254−1261.

(7) For a review of Chloramine-T and related reagents, see: Campbell, M. M.; Johnson, G. *Chem. Rev.* **1978**, *78*, 65−79.

Scheme 2



(19.4/1) for in situ epoxidation of olefin **17** was comparable to the best selectivity obtained by using dioxiranes generated in situ.[8]

II. Mechanistic Study. Several experiments were designed to probe the reactive intermediates of this new in situ epoxidation system. *trans*-Stilbene was treated with 1.1 equiv of Chloramine-M in the presence of 1 equiv of BTEAC in CD_3CN, and the reaction was monitored by ^1H NMR.[9] No *trans*-stilbene oxide was detected after 72 h at room temperature, indicating that although Chloramine-M is an oxidizing reagent, it alone cannot epoxidize *trans*-stilbene. Therefore, we speculated that a reactive oxidizing intermediate might be produced from Chloramine-M and benzaldehyde during the epoxidation reaction.

The higher *cis* to *trans* ratio of (+)-limonene 1,2-epoxides (1.9:1, Table 2, entry 12) observed for our in situ epoxidation of (+)-limonene as compared with the perbenzoic acid case (equal amount of *cis*- and *trans*-1,2-epoxides) suggests that peroxybenzoic acid is unlikely to be the intermediate.[10] As an analogue of Chloramine-T, it is reasonable to wonder if Chloramine-M acts as a source of hypochlorite anion.[7] It was reported by Hamilton et al. that bleach can epoxidize olefins, especially polycyclic aromatic compounds, in the presence of a phase transfer reagent under weakly basic conditions (pH 8−9).[11a] However, the stereochemical outcome of epoxidation with this hypochlorite−PTC system was distinct from that observed with our in situ system. For example, treatment of *cis*-3-hexene with the hypochlorite−PTC system gave a mixture of 75% *cis*-epoxide and 25% *trans*-epoxide,[11b] whereas the *trans*-epoxide was obtained as the major product in our system (Table 2, entry 6). Therefore, the possibility of hypochlorite anion as the epoxidizing agent in our system is also excluded.

When *trans*-stilbene was subjected to our standard in situ epoxidation conditions, it was found that a singlet appeared at 9.0 ppm in the ^1H NMR spectrum of the crude mixture (Figure 1). This singlet was suspected to come from sulfonimine, which was confirmed by the addition of an authentic sample of *trans*-sulfonimine ($MeSO_2N{=}CHPh$) into the above mixture.[12] The presence of sulfonimine ($MeSO_2N{=}CHPh$) in the crude mixture implies that the corresponding *N*-sulfonyloxaziridine might be the oxidant involved in the epoxidation of *trans*-stilbene.

Here we propose a mechanism for the new in situ epoxidation reaction (Scheme 2). As *N*-halogenosulfonamide ion is known

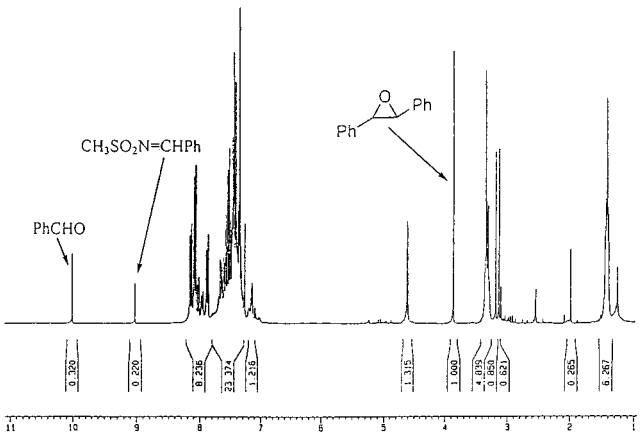
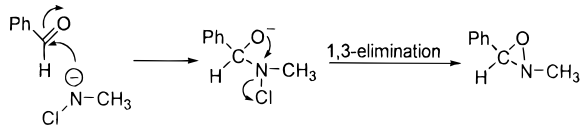


Figure 1. ^1H NMR spectrum (300 MHz) of the crude reaction mixture of *trans*-stilbene (0.1 mmol), Chloramine-M (1.1 equiv), benzaldehyde (4 equiv), and BTEAC (1 equiv) in $CDCl_3$ after aqueous workup.

Scheme 3



to be a nucleophilic reagent,[13] it is reasonable to assume that the nitrogen anion of Chloramine-M attacks benzaldehyde as a nucleophile. The addition product has two possible conformations, **A** and **B**, which are in equilibrium due to the fast pyramidal inversion of the nitrogen atom. Intramolecular S_N2 displacement of **A** and **B** would generate *trans*-*N*-sulfonyloxaziridine **C** and *cis*-*N*-sulfonyloxaziridine **D**, respectively. A similar pathway was proposed by Schmitz et al. to account for the formation of 2-methyl-3-phenyloxaziridine from the reaction of *N*-chloromethylamine with benzaldehyde under alkaline conditions (Scheme 3).[14]

The detection of in situ generated *trans*-*N*-sulfonyloxaziridine **C** and *cis*-*N*-sulfonyloxaziridine **D** by ^1H NMR was attempted. The ^1H NMR spectrum was recorded for the mixture of Chloramine-M (0.11 mmol), benzaldehyde (0.4 mmol), and BTEAC (0.1 mmol) in 2 mL of CD_3CN after 15 h at room

(8) Yang, D.; Jiao, G.-S.; Yip, Y.-C.; Wong, M.-K. *J. Org. Chem.* **1999**, *64*, 1635−1639. For diastereoselective epoxidation of cyclohexene derivatives using isolated dimethyldioxirane, see: Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *J. Org. Chem.* **1996**, *61*, 1830−1841.

(9) The spectra are provided in the Supporting Information.

(10) For epoxidation of (+)-limonene using perbenzoic acid, see: Newhall, W. F. *J. Org. Chem.* **1959**, *24*, 1673.

(11) (a) Krishnan, S.; Kuhn, D. G.; Hamilton, G. A. *J. Am. Chem. Soc.* **1977**, *99*, 8121−8123. (b) Fonouni, H. E.; Krishnan, S.; Kuhn, D. G.; Hamilton, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 7672−7676.

(12) *trans*-*N*-Sulfonimine ($MeSO_2N{=}CHPh$) and *trans*-*N*-sulfonyloxaziridine **C** were prepared according to the literature procedure: Davis, F. A.; Lamendola, J., Jr.; Nadir, U.; Kluger, E. W.; Sedergran, T. C; Panunto, T. W.; Billmers, R.; Jenkins, R., Jr.; Turchi, I. J.; Watson, W. H.; Chen, J. S.; Kimura, M. *J. Am. Chem. Soc.* **1980**, *102*, 2000−2005. The configuration of *trans*-*N*-sulfonyloxaziridine **C** was proved by X-ray analysis (see Supporting Information).

(13) The nucleophilicity of *N*-chlorotoluene-*p*-sulfonamidate anion was found to be comparable to that of the azide anion. See: Hardy, F. E. *J. Chem. Soc. B* **1971**, 1899−1902.

(14) (a) Schmitz, E.; Ohme, R.; Murawski, D. *Angew. Chem.* **1961**, *73*, 708. (b) Schmitz, E. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 333−341.

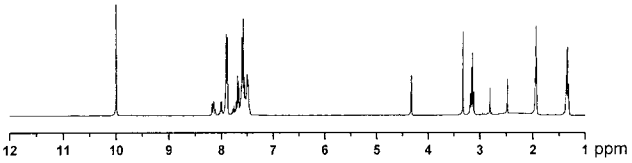


Figure 2. ^{1}H NMR spectrum (300 MHz) of the mixture of Chloramine-M (0.11 mmol), benzaldehyde (0.4 mmol), and BTEAC (0.1 mmol) in CD_3CN (2 mL) at room temperature after 15 h.

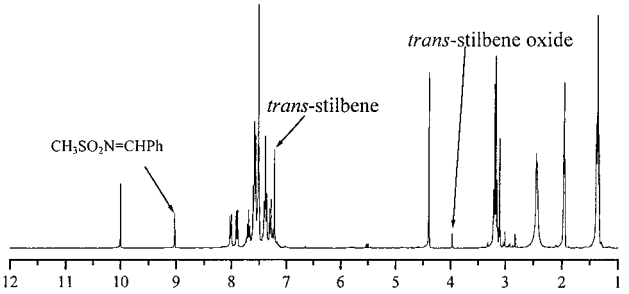


Figure 3. ^{1}H NMR spectrum (300 MHz) of the reaction mixture of *trans*-stilbene (0.1 mmol), *trans*-*N*-sulfonyloxaziridine **C** (1.1 equiv), and BTEAC (1 equiv) in CD_3CN (2 mL) at room temperature after 72 h.

temperature (Figure 2). However, *N*-sulfonyloxaziridines **C** and **D** were not detected by ^{1}H NMR since no peak was found in the range of 5−6 ppm, which is the range at which the signals for benzylic protons of 3-phenyl-*N*-sulfonyloxaziridines usually appear.

We then tried to detect the reaction intermediate by using both electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mass spectrometry techniques in the negative-ion mode. The mass spectra patterns (peaks at *m*/*z* 198 and 199) for the reaction mixture of Chloramine-M (0.11 mmol) and benzaldehyde (0.4 mmol) in 2 mL of CH_3CN, with or without BTEAC (0.1 mmol), were quite similar to that of *trans*-*N*-sulfonyloxaziridine **C** (molecular weight 199).[9] This suggests that *N*-sulfonyloxaziridines **C** and **D** could be the reaction intermediates.

Epoxidation of *trans*-stilbene using 1.1 equiv of *trans*-*N*-sulfonyloxaziridine **C**[12] was then examined in CD_3CN at room temperature.[9] *trans*-*N*-Sulfonyloxaziridine **C** was not destroyed after 72 h, and the yield of *trans*-stilbene oxide was negligible (less than 2% by ^{1}H NMR). Therefore, the possibility of *trans*-*N*-sulfonyloxaziridine **C** as the oxidant for in situ epoxidation of *trans*-stilbene is excluded.

Most interestingly, *trans*-*N*-sulfonyloxaziridine **C** (1.1 equiv) together with BTEAC (1 equiv) did epoxidize *trans*-stilbene at room temperature in CD_3CN (Figure 3), and *trans*-stilbene oxide was isolated in 10% yield with 13% conversion after 72 h. The low conversion is probably because *trans*-**C** could oxidize chloride ion into hypochlorite ion and *N*-sulfonimine ($MeSO_2N$═CHPh) as a side reaction. This is supported by the fact that the amount of *N*-sulfonimine was higher than that of *trans*-stilbene oxide in Figure 3. It was also found that, even in the absence of *trans*-stilbene, *trans*-*N*-sulfonyloxaziridine **C** was completely destroyed by BTEAC within 25 min and benzaldehyde together with *N*-sulfonimine (CH_3SO_2N═CHPh) were detected by ^{1}H NMR.[9]

To further probe the reactive intermediate, diastereoselective epoxidation reactions of 1,3-dimethylcyclohexene were conducted with *trans*-*N*-sulfonyloxaziridine **C** alone, *trans*-*N*-sulfonyloxaziridine **C** together with BTEAC, and our in situ epoxidation system, respectively (Table 5). It was evident that

Table 5. Diastereoselective Epoxidation Reactions of 1,3-Dimethylcyclohexene (**16**)[a]

reaction system	time (h)	convn (%)	yield (%)	*trans*/*cis* epoxide ratio
C[b]	60	54	89	2.8:1
C[b]/BTEAC[c]	24	27	81	4.3:1
Chloramine-M/PhCHO/BTEAC[d]	24	40	83	4.3:1

[a] Reactions were carried out with 0.3 mmol of olefin in 6 mL of anhydrous acetonitrile at room temperature. All the experimental data were obtained by GC analyses. [b] 1.1 equiv. [c] 1 equiv. [d] 1.1 equiv of Chloramine-M, 4 equiv of PhCHO, and 1 equiv of BTEAC.

the latter two reaction systems provided identical diastereoselectivity in epoxidation of 1,3-dimethylcyclohexene, suggesting that they may share the same epoxidizing intermediate despite the lower conversion in the **C**/BTEAC system. *trans*-*N*-Sulfonyloxaziridine **C** gave a lower diastereoselectivitiy, which further supports the conclusion that **C** is not the oxidizing agent in our in situ epoxidation system.

On the basis of these results, we reasoned that BTEAC may have two functions. As a phase transfer reagent, BTEAC improves the solubility of Chloramine-M in CH_3CN. More importantly, chloride anion introduced by BTEAC plays a crucial role in the equilibrium depicted in Scheme 2. Chloride anion can attack the *trans*-*N*-sulfonyloxaziridine **C** at the nitrogen site, yielding conformer **A**.[15] By the pyramidal inversion of the nitrogen atom of **A**, conformer **B** is formed, although it is less favored than **A**. After intramolecular S_N2 displacement, *cis*-*N*-sulfonyloxaziridine **D** is generated. **D** may have higher reactivity than the corresponding *trans*-isomer **C** due to the relatively large steric interactions between the phenyl group and the methylsulfonyl group. Therefore, according to the Curtin−Hammett principle,[16] the reaction may proceed through the minor intermediate **D** if only **D** can epoxidize *trans*-stilbene.[17] There are several examples in the literature that *cis*-2-alkyl-3-phenyloxaziridines showed greater reactivity than the corresponding *trans*-isomers when utilized to oxidize nucleophilic reagents such as amines, sulfides, PhSH, PhSeH, Ph_3P, and Ph_3As.[18]

To the best of our knowledge, there is no literature report on the isolation of *cis*-*N*-sulfonyloxaziridine **D** and its reactivity. Our attempt to isolate **D** also met with failure, which prompted us to investigate the energy difference between **C** and **D**. Theoretical calculations using the Gaussian 94 program[19]

(15) It is also possible that chloride ion attacks the *N*-sulfonyloxaziridines generated in situ at the oxygen site, yielding hypochlorite ion and *N*-sulfonimine ($MeSO_2N$═CHPh). This could not be the major pathway since ClO^- has been excluded as the epoxidizing agent (vide supra) and no sulfonimine was detected in Figure 2.

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(17) In principle, **D** could also be decomposed by BTEAC, similar to the case of **C**. Thus, there are two competing pathways for **D**: reaction with Cl^- and epoxidation. The former pathway mainly gives back **B** but the latter provides the epoxide products. As long as the equilibrium between **C** and **D** is set up and **D** is kinetically competent, according to the Curtin−Hammett principle, epoxide products can be formed. Under our in situ reaction conditions, the concentrations of **C** and **D** at equilibrium were low, which explains why epoxidation reactions were generally slow.

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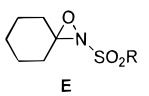
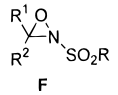
Chart 2



E

R = CH_3
R = 4-$CH_3C_6H_4$
R = 4-BrC_6H_4



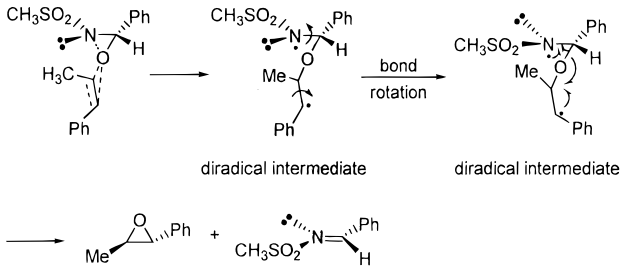
F

R^1 = Et, R^2 = Me
R^1 = $PhCH_2$, R^2 = Me
R^1 = Ph, R^2 = Me

(Hartree−Fock energies determined with the 6-31G* basis set) and Macromodel v. 4.5 program[20] revealed that the ground-state energy of **C** was about 7.6 and 8.2 kcal/mol lower than that of **D**, respectively. As a result of this huge energy gap between **C** and **D**, detection of **D** by ^{1}H NMR even at the equilibrium of **C** and **D** becomes impossible. The ^{1}H NMR spectrum of **C** recorded in CD_3CN at 70 °C showed some partial decomposition products including benzaldehyde and sulfonimine (CH_3SO_2N═CHPh) but no sign of the unfavorable isomer **D** as only one singlet at 5.5 ppm from **C** appeared in the range of 4−6 ppm.[9] In contrast, Jennings et al. reported that the *cis*−*trans* isomerism in 3,3-disubstituted 2-sulfonyloxaziridines **E** and **F (**Chart 2) could be observed by ^{1}H and ^{13}C NMR due to the similar steric interactions in the *cis*- and *trans*-isomers.[21] The 2-alkyl-3-phenyloxaziridines (alkyl groups including methyl, ethyl, isopropyl, and cyclohexyl) isolated in both *cis* and *trans* forms as reported in the literature[18] do not have a tertiary carbon attached to the nitrogen center. In fact, no *cis* form of 2-*tert*-butyl-3-phenyloxaziridine was reported. This suggests that the steric size of the *N*-alkyl substituents affects the relative stability of *cis* and *trans* oxaziridines. We believe the large steric interaction between the phenyl group and the methylsulfonyl group in *cis*-**D** contributes to the significant increase of the energy gap between **C** and **D**.

Theoretical studies by Houk et al. revealed that oxaziridine epoxidation follows a spiro transition state which is highly asynchronous and has an obvious diradical character.[22] A recent study by Beak et al. demonstrated that N−O bond cleavage was more advanced than C−O bond cleavage in the course of the oxygen transfer from *N*-sulfonyloxaziridines to alkenes.[23] Under our in situ conditions, epoxidation of *cis*-olefins gave *trans*-epoxides as the major products, which may be explained

Scheme 4



by invoking diradical intermediates as shown in Scheme 4.[24] Epoxidation of substrates **2** and **4** gave a higher *trans*/*cis* epoxide ratio than **6** (Table 2, entries 2, 4, and 6; Table 3, entries 2−4), probably because the phenyl substituents in the former substrates can significantly stabilize the diradical intermediate compared with the alkyl substituents.

Conclusion

A new epoxidation reaction of various types of olefins has been developed which utilizes a combination of Chloramine-M, benzaldehyde, and BTEAC. *cis*-*N*-Sulfonyloxaziridine **D** is proposed to be the oxidant in the reaction. Synthetic applications of this novel reaction will be explored in the future.

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Supporting Information Available: Experimental Section, ESI-MS and APCI-MS spectra for *trans*-*N*-sulfonyloxaziridine **C** and the mixture of Chloramine-M and benzaldehyde in CH_3-CN with or without BTEAC, ^{1}H NMR spectra (300 MHz) for various experiments done in CD_3CN, and X-ray structural data of *trans*-*N*-sulfonyloxaziridine **C** containing tables of atomic coordinates, thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

JA993472Q

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(24) Epoxidation of *cis*-stilbene by *trans*-*N*-sulfonyloxaziridine **C** was attempted under the conditions reported by Davis and co-workers (Davis, F. A.; Abdul-Malik, N. F.; Awad, S. B.; Harakal, M. E. *Tetrahedron Lett*. **1981**, 917−920). However, it failed to offer any epoxide at 60 °C in $CHCl_3$ even after 16 h. It was found that *cis*-stilbene was completely isomerized to *trans*-stilbene and all **C** decomposed at 60 °C after 16 h. Isomerization of *cis*-stilbene was believed to be caused by $MeSO_3H$ from thermal decomposition of **C**. For a detailed study on the thermal decomposition of *N*-arylsulfonyl-3-phenyloxaziridines, see: Davis, F. A.; Nadir, U. K.; Kluger, E. W. *J. Chem. Soc., Chem. Commun*. **1977**, 25−26.