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# Tetrabutylammonium bisulfate: a new effective catalyst for the hydrolysis of aziridines or epoxides

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$Bu_4NHSO_4$ (TBAHS) is an effective catalyst for the hydrolysis of aziridines and epoxides under mild and non-metal conditions to give the corresponding β-amino alcohols and 1,2-diols in high yields. The catalyst can be recycled.

## Introduction

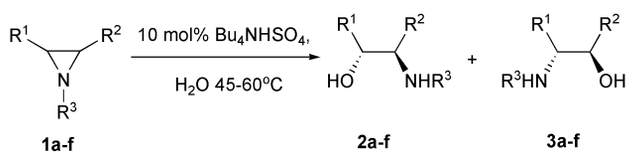
Quaternary ammonium salts are widely used as reagents and catalysts in organic synthesis.[1] For example, quaternary ammonium salts are being extensively utilized as phase transfer catalysts (PTCs) for the transfer of anionic species from aqueous to organic media to facilitate a variety of reactions.[2] Aziridines and epoxides are valuable fine chemicals in organic synthesis due to their facile preparation and stereospecific transformations to other useful products.[3,4] Their ring-opening reactions are usually conducted in the presence of either Lewis acids or strong bases.[5] In addition, 1,2-diols and β-amino alcohols are useful intermediates in organic synthesis. It seems that one of the most convenient ways to obtain these compounds is the hydrolysis of aziridines or epoxides. But there are few reports on such reactions, and in most of the literature, metal salts were needed to realize the reactions.[6] As part of a program aimed at the synthesis of epoxides and aziridines and their applications in organic synthesis,[7] we found that the tetrabutylammonium cation ($Bu_4N^+$) played an important role in the reactions of aziridines with trimethylsilyl compounds.[8] Based upon this finding, further research was conducted to examine the role of quaternary ammonium salts in other reactions of aziridines or epoxides. In this paper, we would like to disclose an efficient procedure for the ring opening of aziridines and epoxides with water in the presence of $Bu_4NHSO_4$ (TBAHS).

## Results and discussion

At the outset, several tetrabutylammonium salts, such as $Bu_4NCl$, $Bu_4NBr$ or $Bu_4NI$, were tested in the reactions of aziridines with allylsilane to see if they affected the ring-opening reactions. However, the ring opening of aziridines by $Cl^-$, $Br^-$ or $I^-$ ion was observed.[2a] To avoid these unexpected reactions, we supposed that it would be important to choose a quaternary ammonium salt with a non-nucleophilic counter ion, for example, $Bu_4NHSO_4$ (TBAHS).[9]

The hydrolysis of an aziridine in the presence of a catalytic amount of $Bu_4NHSO_4$ was examined. Our initial studies showed that $Bu_4NHSO_4$ is an adequate catalyst for the hydrolysis of cyclohexene *N*-tosylaziridine **1a** in water. In the presence of 10 mol% of $Bu_4NHSO_4$, the reaction was conducted at 45 °C for 48 h to provide a single product, *trans*-2-(*N*-tosylamino)cyclohexanol **2a**, in 97% isolated yield. Trace product (5% yield) was obtained in the absence of $Bu_4NHSO_4$. It is worthwhile to note that $Bu_4NHSO_4$ can be recycled. After the extraction of the reaction system by ether, $Bu_4NHSO_4$ was left in water. This aqueous solution of $Bu_4NHSO_4$ can be re-used to conduct the hydrolysis of the aziridine. After three cycles, the yield was still 92% [reaction (1)].

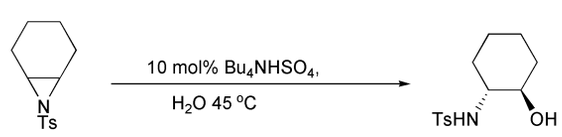
**Table 1** The ring opening of aziridines with water in the presence of $Bu_4NHSO_4$




**1a-f** **2a-f** **3a-f**

| Entry | Substrate | $R^1$, $R^2$, $R^3$ | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 | **1a** | $-(CH_2)_4-$, Ts | **2a** | 97 |
| 2 | **1b** | $-(CH_2)_4-$, Bz | **2b** | 96 |
| 3 | **1c** | $-(CH_2)_3-$, Ts | **2c** | 98 |
| 4 | **1d** | $-(CH_2)_5-$, Ts | **2d** | 75 |
| 5 | **1e** | Ph, H, Ts | **2e**, **3e** | 99 (> 95 : 5)[b] |
| 6 | **1f** | $C_4H_9$, H, Ts | **2f**, **3f** | 87 (41 : 59)[b] |

[a] Isolated yield. [b] The ratio of isomers was determined by $^1H$ NMR.




**1a** **2a** (1)

$Bu_4NHSO_4$: cycle 1: Yield : 97%
cycle 2: Yield : 98%
cycle 3: Yield : 92%

Various aziridines were used to test the catalytic ability of $Bu_4NHSO_4$ (Table 1). In most cases, aziridines were hydrolyzed to give rise to the corresponding β-amino alcohols in high yields. Acyclic terminal aziridines **1e** and **1f** gave information about the regiochemistry of the reaction. The aziridine **1e** led to the formation of one regioisomer, incorporating the hydroxyl group at the phenyl-substituted carbon, as expected for a charge-controlled ring-opening process (Entry 5, Table 1).[10] However, for the alkyl-substituted aziridine **1f**, two products **2f** and **3f** were formed in a ratio of 41 : 59, which reflects the expected competition of opening pathways for this type of aziridine (Entry 6, Table 1). At lower temperature, a more sluggish reaction took place.

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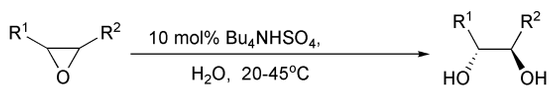
**Table 2** The hydrolysis of epoxides in the presence of $Bu_4NHSO_4$




**4a-g** **5a-g**

| Entry | Substrate | $R^1$, $R^2$ | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 | **4a** | $-(CH_2)_4-$ | **5a** | 97 |
| 2 | **4b** | $-(CH_2)_3-$ | **5b** | 98 |
| 3 | **4c** | $-(CH_2)_6-$ | **5c** | 61 |
| 4 | **4d** | Ph, H | **5d** | 97 |
| 5 | **4e** | n-$C_4H_9$, H | **5e** | 98 |
| 6 | **4f** | $CH_2CHCH_2CH_2$, H | **5f** | 96 |
| 7 | **4g** | $ClCH_2$, H | **5g** | 94 |

[a] Isolated yield based on epoxide.

$Bu_4NHSO_4$ is also an effective catalyst for the hydrolysis of epoxides. It can be seen from Table 2 that various epoxides could be hydrolyzed to give 1,2-diol in good to excellent yields using $Bu_4NHSO_4$ as a catalyst. In the case of the less reactive epoxide **4c**, the reaction also took place smoothly to give product **5c** in moderate yield. No influence of the functional groups on the reaction was observed (Entries 6 and 7, Table 2). Control experiments showed that lower yields (< 10%) were obtained in the absence of $Bu_4NHSO_4$.

When 20 mol% of NaOH was used instead of $Bu_4NHSO_4$, the reaction of **1a** with water proceeded sluggishly at 60 °C to give **2a** in 13% yield, however the yield was raised to 73% with the increase of the amount of NaOH to 200 mol%. When 10 mol% $NaHSO_4$ or $Bu_4NNO_3$ was used, product **2a** was isolated in 51% and 39% yield, respectively. For comparison, a 97% yield of **2a** was obtained in the presence of 10 mol% $Bu_4NHSO_4$ under the same conditions. In accordance with these results and the regiochemistry of the reaction of **1e**, we propose that $Bu_4NHSO_4$ might play a role as a mild Lewis acid in the reactions.

## Conclusion

Tetrabutylammonium bisulfate (TBAHS) is an efficient and recyclable catalyst for the hydrolysis of aziridines or epoxides under neutral and non-metal conditions. The reactions provide β-amino alcohols and 1,2-diols in a simple and convenient way, which offers new promise of an economic and environmentally benign process. Further investigations on the asymmetric version of the reactions and the applications of $Bu_4NHSO_4$ as a catalyst in other reactions are in progress.

## Experimental

The commercially available reagents were used as received without further purification. Melting points are uncorrected. $^1$H NMR spectra were recorded on a 300 MHz spectrometer and the chemical shifts were referenced to $CHCl_3$ ($\delta$ 7.27) in $CDCl_3$. Chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard. IR spectra were measured in $cm^{-1}$, using a Shimadzu IR-440 infrared spectrophotometer. Mass spectra were taken using HP5989A and Finnigan MAT mass spectrometers, respectively. Elemental analyses were performed on a Foss-Heraeus Vario EL instrument.

### General procedure

To a stirred solution of aziridine **1** or epoxide **4** (0.5 mmol) in $H_2O$ (2.0 ml) was added $Bu_4NHSO_4$ (17 mg, 0.05 mmol) and the resulting mixture was stirred at the appropriate temperature for 24–48 h. The mixture was extracted with $Et_2O$ (3 × 10 ml), the organic layer was combined and dried over $Na_2SO_4$. Then the solvent was removed in vacuum and the crude product was purified by flash column chromatography to provide the corresponding product.

The aqueous solution of $Bu_4NHSO_4$ was re-used and the product **2a** was obtained in 98% yield.

***trans*-2-(*N*-Tosylamino)-1-cyclohexanol (2a).** $^1$H NMR (300 MHz, $CDCl_3$): 1.15–1.29 (m, 4H), 1.58–1.61 (m, 1H), 1.66–1.77 (m, 2H), 2.01–2.05 (m, 1H), 2.42 (s, 3H), 2.68 (d, $J$ = 3.0 Hz, 1H), 2.83–2.91 (m, 1H), 3.26–3.34 (m, 1H), 4.95 (d, $J$ = 7.2 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 2H), 7.80 (d, $J$ = 8.7 Hz, 2H); IR (film): $\tilde{\nu}$ = 3547, 3270, 1599, 1458 $cm^{-1}$; EI-MS: *m*/*z* (%): 269 ($M^+$, 0.76), 155 (15), 114 (28), 91 (100); Anal. for $C_{13}H_{19}NO_3S$: Calcd.: C, 57.97; H, 7.11; N, 5.20. Found: C, 58.00; H, 6.90; N, 5.07%.

***trans*-2-(*N*-Phenylcarbonylamino)-1-cyclohexanol (2b).** $^1$H NMR (300 MHz, $CDCl_3$) 1.21–1.44 (m, 4H), 1.72–1.76 (m, 2H), 2.05–2.10 (m, 2H), 3.40–3.48 (m, 1H), 3.70 (d, $J$ = 4.8 Hz, 1H), 3.78–3.89 (m, 1H), 6.32 (d, $J$ = 5.7 Hz, 1H), 7.40–7.54 (m, 3H), 7.77–7.80 (m, 2H); IR (film): $\tilde{\nu}$ = 3479, 3298, 3064, 1629, 1578 $cm^{-1}$; EI-MS: *m*/*z* (%): 219 ($M^+$, 0.7), 191 (1.7), 122 (36), 105 (100); Anal. for $C_{13}H_{17}NO_2$: Calcd.: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.96; H, 7.65; N, 6.14%.

***trans*-2-(*N*-Tosylamino)-1-cyclopentanol (2c).** $^1$H NMR (300 MHz, $CDCl_3$): 1.32–1.45 (m, 1H), 1.56–2.02 (m, 6H), 2.42 (s, 3H), 3.18–3.27 (m, 1H), 4.03–4.10 (m, 1H), 4.83 (d, $J$ = 5.7 Hz, 1H), 7.33 (d, $J$ = 7.8 Hz, 2H), 7.80 (d, $J$ = 7.9 Hz, 2H); IR (film): $\tilde{\nu}$ = 3463, 3178, 1598, 1498 $cm^{-1}$; EI-MS: *m*/*z* (%): 255 ($M^+$, 0.2), 238 (0.6), 155 (12), 100 (100); Anal. for $C_{12}H_{17}NO_3S$: Calcd.: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.58; H, 6.78; N, 5.37%.

***trans*-2-(*N*-Tosylamino)-1-cycloheptanol (2d).** $^1$H NMR (300 MHz, $CDCl_3$) 1.15–1.87 (m, 10H), 2.43 (s, 3H), 2.61–2.70 (m, 1H), 2.95–3.07 (m, 1H), 3.44–3.52 (m, 1H), 5.00 (d, $J$ = 7.5 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 2H), 7.80 (d, $J$ = 8.9 Hz, 2H); IR (film): $\tilde{\nu}$ = 3452, 3141, 1599, 1498 $cm^{-1}$; EI-MS: *m*/*z* (%): 283 ($M^+$, 0.67), 155 (17), 128 (100); Anal. for $C_{14}H_{21}NO_3S$: Calcd.: C, 59.34; H, 7.47; N, 4.94. Found: C, 59.33; H, 7.32; N, 4.79%.

**2-(*N*-Tosylamino)-1-phenyl-1-ethanol (2e).** $^1$H NMR (300 MHz, $CDCl_3$): 2.41 (s, 3H), 2.96–3.05 (m, 1H), 3.18–3.27 (m, 1H), 4.79 (dd, $J$ = 8.7, 3.6 Hz, 1H), 5.18–5.22 (m, 1H), 7.24–7.35 (m, 7H), 7.73 (d, $J$ = 8.4 Hz, 2H); IR (film): $\tilde{\nu}$ = 3410, 3158, 3033, 1599 $cm^{-1}$; EI-MS: *m*/*z* (%): 293 ($M^+$, 0.6), 275 (1), 184 (13), 155 (37), 107 (100); Anal. for $C_{15}H_{17}NO_3S$: Calcd.: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.99; H, 6.01; N, 4.73%.

**1-(*N*-Tosylamino)-2-hexanol (2f).** $^1$H NMR (300 MHz, $CDCl_3$): 0.89–0.91 (m, 3H), 1.23–1.44 (m, 6H), 2.22 (br, 1H), 2.44 (s, 3H), 2.74–2.83 (m, 1H), 3.04–3.12 (m, 1H), 3.66–3,69 (m, 1H), 5.10–5.13 (m, 1H), 7.33 (d, $J$ = 8.6 Hz, 2H), 7.77 (d, $J$ = 8.8 Hz, 2H); IR (film): $\tilde{\nu}$ = 3498, 3284, 1599, 1496 $cm^{-1}$; EI-MS: *m*/*z* (%): 272 ($M - H^+$, 0.7), 240 (78), 155 (64), 91 (100); Anal. for $C_{13}H_{21}NO_3S$: Calcd.: C, 57.54; H, 7.80; N, 5.16. Found: C, 57.16; H, 7.53; N, 4.91%.

**2-(*N*-Tosylamino)-1-hexanol (3f).** $^1$H NMR (300 MHz, $CDCl_3$): 0.87–0.91 (m, 3H), 1.02–1.43 (m, 6H), 2.04–2.07 (m, 1H), 2.42 (s, 3H), 3.19–3.24 (m, 1H), 3.45–3.47 (m, 1H), 3.53–3.58 (m, 1H), 4.76 (d, $J$ = 7.5 Hz, 1H), 7.28 (d, $J$ = 8.6 Hz, 2H), 7.78 (d, $J$ = 8.6 Hz, 2H); IR (film): $\tilde{\nu}$ = 3495, 3285 $cm^{-1}$; EI-MS: *m*/*z* (%): 272 ($M - H^+$, 0.7), 240 (95), 155 (64), 91 (100); Anal. for $C_{13}H_{21}NO_3S$: Calcd.: C, 57.54; H, 7.80; N, 5.16. Found: C, 57.58; H, 7.57; N, 4.98%.

***trans*-1,2-Cyclohexanediol (5a).**[11] $^1$H NMR (300 MHz, $CDCl_3$): 1.23–1.30 (m, 4H), 1.69–1.72 (m, 2H), 1.93–2.00 (m, 2H), 3.06 (m, 2H), 3.35 (br, 2H); EI-MS: *m*/*z* (%): 116 ($M^+$, 36).

***trans*-1,2-Cyclopentanediol (5b).**[12] $^1$H NMR (300 MHz, $CDCl_3$): 1.45–1.58 (m, 2H), 1.60–1.76 (m, 2H), 1.94–2.06 (m, 2H), 3.43 (br, 2H), 3.92–4.00 (m, 2H); EI-MS: *m*/*z* (%): 102 ($M^+$, 65).

***trans*-1,2-Cyclooctanediol (5c).**[13] $^1$H NMR (300 MHz, $CDCl_3$): 1.25–1.74 (m, 10H), 1.82–1.91 (m, 2H), 2.81 (br, 2H), 3.56–3.61 (m, 2H); EI-MS: *m*/*z* (%): 144 ($M^+$, 55).

**1-Phenyl-1,2-ethanediol (5d).**[14] $^1$H NMR (300 MHz, $CDCl_3$): 2.67 (br, 1H), 3.09 (br, 1H), 3.62–3.78 (m, 2H), 4.79–4.84 (m, 1H), 7.27–7.39 (m, 5H); EI-MS: *m*/*z* (%): 138 ($M^+$, 48).

**1,2-Hexanediol (5e).**[15] $^1$H NMR (300 MHz, $CDCl_3$): 0.91 (t, $J$ = 6.9 Hz, 3H), 1.28–1.46 (m, 6H), 3.27 (br, 2H), 3.38–3.45 (m, 1H), 3.61–3.68 (m, 2H); EI-MS: *m*/*z* (%): 118 ($M^+$, 24).

**5-Hexene-1,2-diol (5f).**[16] $^1$H NMR (300 MHz, $CDCl_3$): 1.48–1.58 (m, 2H), 2.08–2.27 (m, 2H), 2.88–2.96 (m, 2H), 3.40–3.47 (m, 1H), 3.66–3.74 (m, 2H), 4.96–5.10 (m, 2H), 5.76–5.90 (m, 1H); EI-MS: *m*/*z* (%): 116 ($M^+$, 75).

**3-Chloro-1,2-propanediol (5g).**[17] $^1$H NMR (300 MHz, $CDCl_3$): 3.08 (br, 1H), 3.50–3.52 (m, 1H), 3.54–3.69 (m, 3H), 3.70 (br, 1H), 3.74–3.78 (M, 1H); EI-MS: *m*/*z* (%): 112 ($M^+$, 13), 110 ($M^+$, 39).

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