

# Novel S<sub>N</sub>2 ring-opening reactions of 2- and 2,2-substituted thiiranes with thiols using Na<sup>+</sup>-exchanged X-type zeolite or triethylamine in methanol



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A regiospecific ring-opening reaction occurs at the C-3 of 2-methyl- and 2,2-dimethyl-thiiranes **1a** and **1b** upon treatment of **1a** and **1b** with thiols **2** using Na<sup>+</sup>-exchanged X-type zeolite (Na<sup>+</sup>-zeolite X) or Et<sub>3</sub>N in MeOH to yield alkylthioethanethiols **3**. However, the reaction of 2-phenylthiirane **1c** is no longer regiospecific, giving **3** and **4** by the ring-openings at C-3 and C-2. The yield of the products is influenced by the catalyst, the solvent polarity, the concentration and nucleophilicity of **2**, the reactivity of **1** towards **2** and so on. This suggests that the reactions using Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N proceed *via* a zwitterion or an ion-pair intermediate, respectively, by an S<sub>N</sub>2 attack on **1** of **2**, having enhanced nucleophilicity due to the basic catalysts. The reactions using Na<sup>+</sup>-zeolite A-3 or H<sup>+</sup>-zeolite X in MeOH or benzene and that using H<sub>2</sub>SO<sub>4</sub> in benzene are also investigated.

The use of zeolites as catalysts in various organic transformations has been a field of growing importance.<sup>1-10</sup> The excellent catalytic activity of zeolites can be attributed to the large surfaces, acidic and/or basic sites present on the surface, the intracrystalline pore structure, *etc.*

In the absence of catalysts, thiiranes react rather sluggishly with thiols; for example, upon heating cyclohexene sulfide with EtSH for 6 h at 120 °C, almost all of the starting material was recovered unchanged.<sup>11</sup> The ring-opening reaction of 2,2-dimethylthiirane **1b** with thiols in the presence of a catalytic amount of NaOEt or BF<sub>3</sub> etherate has been reported to produce non-regiospecifically **3** and **4** which are formed by attacks at the C-3 and C-2 of **1**, respectively.<sup>12,13</sup> The catalytic reaction of unsubstituted thiirane, 2-methylthiirane **1a** or 2-phenylthiirane **1c** with thiols has not furnished good yields of the corresponding **3** or **4** because of contamination by other products, such as **5**, formed by an attack of **3** or **4** on **1**.<sup>14-16</sup> We here describe that the ring-opening reactions of thiiranes **1a-c** with thiols efficiently occur by an S<sub>N</sub>2 mechanism using a catalytic quantity of Na<sup>+</sup>-exchanged X-type zeolite (Na<sup>+</sup>-zeolite X) or Et<sub>3</sub>N in polar MeOH, leading to the regiospecific formation of **3** using **1a** and **1b** although the use of **1c** gives **3** and **4** non-regiospecifically.

## Results and discussion

### Ring-opening reactions of 2-methyl-, 2,2-dimethyl- and 2-phenylthiiranes **1a-c** with alkylthiols **2a-d** using Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N

**Regioselectivity of the ring-opening reactions.** Ring-opening reactions of **1a** or **1b** with EtSH **2a** and *n*-BuSH **2b** using Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N in MeOH gave 1-(alkylthio)propane-2-thiols **3a,a** and **3a,b** or **3b,a** and **3b,b** by a regiospecific attack of **2** at the C-3 of **1** along with a 2:1 addition product **5** (Table 1). In contrast, the reaction of **1c** with **2a** produced non-regiospecifically **3c,a** and **4c,a** by attacks of **2a** at the C-3 and C-2 of **1c** (Table 2); the yield of **4** was higher than **3**. The results correspond well with those from a so-called borderline S<sub>N</sub>2 mechanism in which the reactions obey S<sub>N</sub>2 kinetics, but are controlled by electronic and steric factors on bond-breaking: the regiospecific ring-opening at the less crowded C-3 of **1a** and **1b** clearly indicates that the reaction proceeds by the S<sub>N</sub>2 mech-

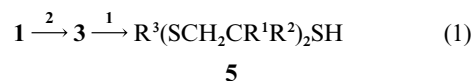
**Table 1** Ring-opening reactions of 2-methyl- and 2,2-dimethylthiiranes **1a** and **1b** (4.0 mmol) with alkylthiols **2a-d** in MeOH (8.0 cm<sup>3</sup>) at 25 °C for 24 h

| Thiirane  | R of RSH <b>2</b>              | 2/mmol | Catalyst (180 mg)            | Yield <sup>a</sup> (%) |          |
|-----------|--------------------------------|--------|------------------------------|------------------------|----------|
|           |                                |        |                              | <b>3</b>               | <b>5</b> |
| <b>1a</b> | <b>a</b> ; R = Et              | 20     | Na <sup>+</sup> -zeolite X   | 52                     | 1.5      |
| <b>1a</b> | <b>a</b> ; R = Et              | 20     | Na <sup>+</sup> -zeolite A-3 | 45                     | 4.3      |
| <b>1a</b> | <b>a</b> ; R = Et              | 20     | Et <sub>3</sub> N            | 54                     | 7.1      |
| <b>1a</b> | <b>a</b> ; R = Et              | 20     | None                         | 3.9                    | 0        |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup> | 4.0    | Na <sup>+</sup> -zeolite X   | 22                     | 14       |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup> | 12     | Na <sup>+</sup> -zeolite X   | 60                     | 14       |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | Na <sup>+</sup> -zeolite X   | 70                     | 14       |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | Na <sup>+</sup> -zeolite A-3 | 45                     | 2.5      |
| <b>1a</b> | <b>c</b> ; R = Bu <sup>s</sup> | 20     | Na <sup>+</sup> -zeolite X   | 44                     | 20       |
| <b>1a</b> | <b>d</b> ; R = Bu <sup>t</sup> | 20     | Na <sup>+</sup> -zeolite X   | 14                     | 0        |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | Et <sub>3</sub> N            | 71                     | 13       |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup> | 4.0    | None                         | 1.5                    | 0        |
| <b>1b</b> | <b>a</b> ; R = Et              | 20     | Na <sup>+</sup> -zeolite X   | 67                     | —        |
| <b>1b</b> | <b>a</b> ; R = Et              | 20     | Na <sup>+</sup> -zeolite A-3 | 59                     | —        |
| <b>1b</b> | <b>a</b> ; R = Et              | 20     | Et <sub>3</sub> N            | 72                     | —        |
| <b>1b</b> | <b>a</b> ; R = Et              | 20     | None                         | 27                     | —        |
| <b>1b</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | Na <sup>+</sup> -zeolite X   | 60                     | —        |
| <b>1b</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | Na <sup>+</sup> -zeolite A-3 | 24                     | —        |
| <b>1b</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | Et <sub>3</sub> N            | 69                     | —        |
| <b>1b</b> | <b>b</b> ; R = Bu <sup>n</sup> | 4.0    | None                         | 5.2                    | —        |
| <b>1b</b> | <b>b</b> ; R = Bu <sup>n</sup> | 20     | None                         | 54                     | —        |

<sup>a</sup> The yields are based on the amount of thiiranes **1a** and **1b** used.

anism. On the other hand, electronic factors may be involved in the reaction of **1c** to give **4** *via* an S<sub>N</sub>2 transition state possessing a partial benzylic cation, while steric factors lead to the production of **3**. The following results support the S<sub>N</sub>2 mechanism well.

By-products **5a-c** can be formed by reaction of two molecules of **1** with one molecule of **2** *via* **3** [eqn. (1)]. Only in the



reaction of **1a** with **2a-c**, can **5** be produced (Tables 1 and 3). **2a-c** are less reactive than **2e** and **2f** (as shown below), and this

**Table 2** Ring-opening reaction of 2-phenylthiirane **1c** (4.0 mmol) with EtSH **2a** in MeOH (8.0 cm<sup>3</sup>) at 25 °C for 2 h

| 2a/mmol | Catalyst (180 mg)          | Yield <sup>a</sup> (%) |      |
|---------|----------------------------|------------------------|------|
|         |                            | 3c,a                   | 4c,a |
| 4.0     | Na <sup>+</sup> -zeolite X | 2.9                    | 9.1  |
| 20      | Na <sup>+</sup> -zeolite X | 7.3                    | 17   |
| 40      | Na <sup>+</sup> -zeolite X | 17                     | 51   |
| 4.0     | Et <sub>3</sub> N          | 1.9                    | 6.1  |
| 20      | Et <sub>3</sub> N          | 9.3                    | 21   |
| 40      | Et <sub>3</sub> N          | 23                     | 50   |
| 4.0     | None                       | 1.1                    | 3.3  |

<sup>a</sup> The yields are based on the amount of **1c** used.

**Table 3** Effect of solvent-polarity for ring-opening reaction of 2-methylthiirane **1a** (4.0 mmol) with *n*-BuSH **2b** (20 mmol) using Na<sup>+</sup>-zeolite X (180 mg) in solvent (8.0 cm<sup>3</sup>) at 25 °C for 24 h

| Solvent                         | Yield <sup>a</sup> (%) |       |
|---------------------------------|------------------------|-------|
|                                 | 3a,b                   | 5a,b  |
| MeOH                            | 70                     | 14    |
| EtOH                            | 45                     | 6.3   |
| <i>n</i> -PrOH                  | 6.8                    | Trace |
| <i>n</i> -BuOH                  | 5.4                    | 0     |
| CH <sub>2</sub> Cl <sub>2</sub> | 1.2                    | 0     |
| EtOEt                           | 1.2                    | 0     |
| PhH                             | 3.4                    | 0     |

<sup>a</sup> The yields are based on the amount of **1a** used.

allows **3** to react with **1**. The nucleophilic products **3a,a–c** from the reaction of **1a** with **2a–c** are less sterically hindered than those from the reaction of **1b** and **1c** with **2a–c**, thus allowing them to react again with **1** to form **5**.

**Effect of the catalyst on the nucleophilicity of 2.** The yield of **3** and **4** in the reactions of **1a–c** in MeOH was markedly lower in the absence of Na<sup>+</sup>-zeolite or Et<sub>3</sub>N in MeOH than in its presence (Tables 1 and 2). This suggests that the nucleophilicity of **2** is enhanced by the interaction of the thiol hydrogen in **2** with the basic site of the catalyst. Thus, the reactions may occur by the S<sub>N</sub>2 mechanism (Schemes 1 and 2) which is affected by the nucleophilicity. The interaction with the zeolite has been proposed by our studies.<sup>17–20</sup>

**Effect of the solvent polarity.** The yield of **3a,b** (or the total yield of **3a,b** and **5a,b**) in the reaction of **1a** with **2b** using Na<sup>+</sup>-zeolite X increased with an increase in solvent polarity (Table 3). The yield of the products in the reactions of **1b** or **1c** using Na<sup>+</sup>-zeolite X was also enhanced when the polar solvent MeOH was used instead of benzene (Tables 1, 2 and 4). These facts suggest that the reactions of **1** with **2** using Na<sup>+</sup>-zeolite X proceed *via* a zwitterion intermediate because a more polar solvent can better stabilise the intermediate by solvation, giving the products after a fast proton-shift (Scheme 1). The yield of **3a,b** in benzene is a little higher than that in CH<sub>2</sub>Cl<sub>2</sub> or EtOEt (Table 3). We may consider that the zwitterion intermediate is somewhat stabilised as an intimate ion-pair in the pores of the Na<sup>+</sup>-zeolite X in non-polar benzene as described below, leading to this result.

The reaction of **1a–c** was completely suppressed using Et<sub>3</sub>N in benzene, but occurred efficiently using Et<sub>3</sub>N in MeOH (Tables 1, 2 and 4). This implies that the reaction of **1** with **2** using Et<sub>3</sub>N proceeds *via* an ion-pair intermediate (Scheme 2); the intermediate cannot be stabilised as an intimate ion-pair in benzene owing to steric hindrance by the triethyl group in Et<sub>3</sub>N thus giving no products, but can be stabilised by solvation in MeOH to afford the products.

**Table 4** Ring-opening reactions of thiiranes **1a–c** (4.0 mmol) with thiol **2a** or **2b** using Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N in benzene (8.0 cm<sup>3</sup>) at 25 °C for 24 h

| Thiirane  | R of RSH <b>2</b>      | 2/mmol | Catalyst (180 mg)            | Yield <sup>a</sup> (%) |   |
|-----------|------------------------|--------|------------------------------|------------------------|---|
|           |                        |        |                              | 3                      | 5 |
| <b>1a</b> | a; R = Et              | 20     | Na <sup>+</sup> -zeolite X   | 29                     | 0 |
| <b>1a</b> | a; R = Et              | 20     | Na <sup>+</sup> -zeolite A-3 | 0                      | 0 |
| <b>1a</b> | a; R = Et              | 20     | Et <sub>3</sub> N            | 0                      | 0 |
| <b>1a</b> | b; R = Bu <sup>n</sup> | 20     | Na <sup>+</sup> -zeolite X   | 3.4                    | 0 |
| <b>1a</b> | b; R = Bu <sup>n</sup> | 20     | Et <sub>3</sub> N            | 0                      | 0 |
| <b>1b</b> | a; R = Et              | 20     | Na <sup>+</sup> -zeolite X   | 28                     | — |
| <b>1b</b> | a; R = Et              | 20     | Na <sup>+</sup> -zeolite A-3 | 0                      | — |
| <b>1b</b> | a; R = Et              | 20     | Et <sub>3</sub> N            | 0                      | — |
| <b>1b</b> | b; R = Bu <sup>n</sup> | 20     | Na <sup>+</sup> -zeolite X   | 0                      | — |
| <b>1b</b> | b; R = Bu <sup>n</sup> | 20     | Et <sub>3</sub> N            | 0                      | — |
| <b>1c</b> | a; R = Et              | 4.0    | Na <sup>+</sup> -zeolite X   | 0 <sup>b</sup>         | — |
| <b>1c</b> | a; R = Et              | 4.0    | Et <sub>3</sub> N            | 0 <sup>b</sup>         | — |

<sup>a</sup> The yields are based on the amount of **1** used. <sup>b</sup> In this case, **4c,a** is also not formed.

**Effects of the concentration and nucleophilicity of 2.** The yield of **3** and **4** in the reactions of **1a–c** with **2a** or **2b** using Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N in MeOH increased with increasing concentration of **2** (Tables 1 and 2); in fact, **1a** and **1b** were not reactive in the absence of **2**. In the reactions of **1a** with *n*-, *sec*- and *tert*-butylthiols **2b–d**, the yield of **3** was decreased with the decreasing nucleophilicity of **2** (*i.e.* **2b** > **2c** > **2d**) because of the bulkiness of the alkyl group of **2** (Table 1). These observations support well the proposed S<sub>N</sub>2 mechanism for the reaction. The formation of **4** from **1c** initially seems to occur *via* an S<sub>N</sub>1 mechanism, considering the facile possible formation of a stable benzylic cation on the C-2–S breaking of **1c**. However, the fact (see Table 2) that the yield of **4** increases in the presence of the Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N basic catalyst and with the enhanced amount of **2** clearly rules out the S<sub>N</sub>1 mechanism.

**Relative reactivity of 1a–c.** The relative reactivity (giving **3** or a mixture of **3** and **4**) of **1a–c** with **2a** was found to be **1b** > **1a** > **1c**. Thiirane **1b** might be more reactive than **1a** because **1b**, with two methyl groups, can relieve a higher ring-strain *via* the S<sub>N</sub>2 ring-opening than **1a** with only one methyl group. We infer that the ring-opening of **1c** is less favoured due to a resonance-stabilisation effect between the phenyl π-electron and the three-membered ring electron with a partial π-character.

**Stabilisation as an intimate ion-pair.** No products were formed in the reactions of **1a–c** with **2a** or **2b** using Et<sub>3</sub>N in benzene as shown above. However, the reaction of **1a** or **1b** with **2a** using Na<sup>+</sup>-zeolite X in benzene could give **3** in 29 or 28% yield, respectively (Table 4). On the contrary, the reaction using **2b** instead of **2a** led to less or no production of **3** (Table 4). The zwitterion intermediate (in Scheme 1) in the reaction with **2a** can be stabilised as the intimate ion-pair in benzene to give **3** while this stabilisation is hindered in the reaction with **2b** owing to the butyl group in **2b** being bulkier than the ethyl group in **2a**.

#### Pore reactions

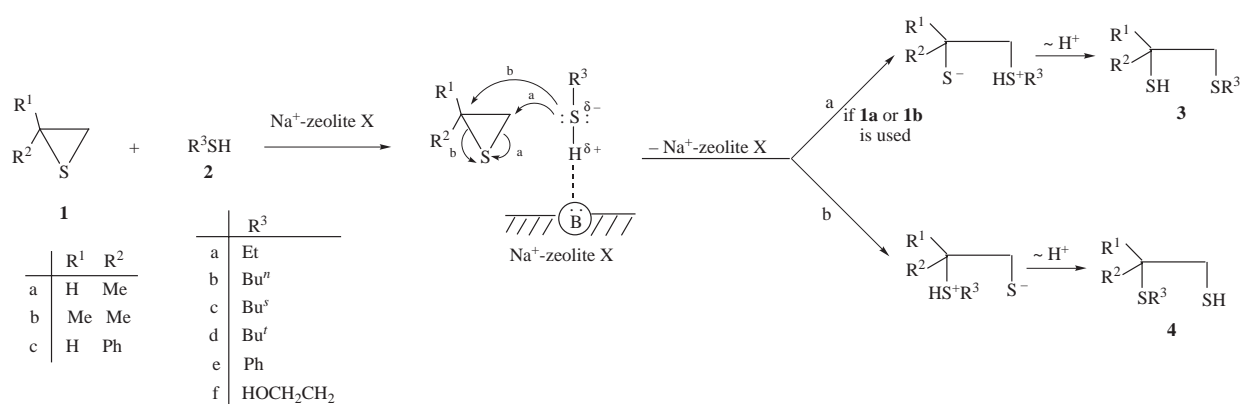
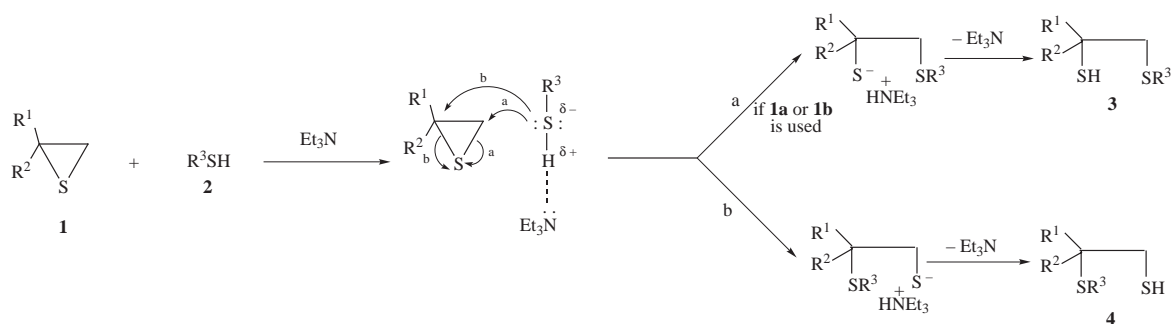
The yield of **3** in the reactions of **1a** and **1b** in MeOH was low when Na<sup>+</sup>-zeolite A-3 (minimum pore diameter 3 Å) was used compared with the reactions when Na<sup>+</sup>-zeolite X (minimum pore diameter 10 Å) was used (Table 1). This shows that Na<sup>+</sup>-zeolite A-3 is active only on the surface whereas Na<sup>+</sup>-zeolite X is active not only on the surface but also in the pores.

The formation of **3a,a** or **3b,a** in the reaction of **1a** or **1b** with **2a** was completely suppressed using Na<sup>+</sup>-zeolite A-3 in benzene although this formation occurs in *ca.* 30% yield using Na<sup>+</sup>-zeolite X in benzene as described above. This indicates that the

**Table 5** Ring-opening reactions of thiiranes **1a** and **1b** (4.0 mmol) with PhSH **2e** or HOCH<sub>2</sub>CH<sub>2</sub>SH **2f** at 25 °C for 24 h

| Thiirane  | R of RSH <b>2</b>                         | <b>2</b> /mmol | Catalyst (180 mg)          | Solvent (8.0 cm <sup>3</sup> ) | Yield <sup>a</sup> (%) <b>3</b> |
|-----------|---|----------------|----------------------------|--------------------------------|---------------------------------|
| <b>1a</b> | e; R = Ph                                 | 4.0            | Na <sup>+</sup> -zeolite X | MeOH                           | 71                              |
| <b>1a</b> | e; R = Ph                                 | 4.0            | Na <sup>+</sup> -zeolite X | PhH                            | 0                               |
| <b>1a</b> | e; R = Ph                                 | 4.0            | Et <sub>3</sub> N          | MeOH                           | 66                              |
| <b>1a</b> | e; R = Ph                                 | 40             | Na <sup>+</sup> -zeolite X | MeOH                           | 77                              |
| <b>1a</b> | e; R = Ph                                 | 40             | Et <sub>3</sub> N          | MeOH                           | 79                              |
| <b>1a</b> | e; R = Ph                                 | 40             | None                       | MeOH                           | 14                              |
| <b>1a</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 4.0            | Et <sub>3</sub> N          | MeOH                           | 51                              |
| <b>1a</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Na <sup>+</sup> -zeolite X | MeOH                           | 71                              |
| <b>1a</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Na <sup>+</sup> -zeolite X | PhH                            | 0                               |
| <b>1a</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Et <sub>3</sub> N          | MeOH                           | 73                              |
| <b>1a</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Et <sub>3</sub> N          | PhH                            | 12                              |
| <b>1a</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | None                       | MeOH                           | 7.4                             |
| <b>1b</b> | e; R = Ph                                 | 4.0            | Na <sup>+</sup> -zeolite X | MeOH                           | 56                              |
| <b>1b</b> | e; R = Ph                                 | 4.0            | Na <sup>+</sup> -zeolite X | PhH                            | 0                               |
| <b>1b</b> | e; R = Ph                                 | 4.0            | Et <sub>3</sub> N          | MeOH                           | 51                              |
| <b>1b</b> | e; R = Ph                                 | 4.0            | Et <sub>3</sub> N          | PhH                            | 13                              |
| <b>1b</b> | e; R = Ph                                 | 4.0            | None                       | MeOH                           | 56                              |
| <b>1b</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Na <sup>+</sup> -zeolite X | MeOH                           | 49                              |
| <b>1b</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Na <sup>+</sup> -zeolite X | PhH                            | 0                               |
| <b>1b</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Et <sub>3</sub> N          | MeOH                           | 57                              |
| <b>1b</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | Et <sub>3</sub> N          | PhH                            | 3.8                             |
| <b>1b</b> | f; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | None                       | MeOH                           | 55                              |

<sup>a</sup> The yields are based on the amount of **1** used.

**Scheme 1****Scheme 2**

zwitterion intermediate (in Scheme 1) in benzene can be stabilised as the intimate ion-pair in the pores of Na<sup>+</sup>-zeolite X, but not on the surface of the zeolite. This type of stabilisation in the pore is an interesting development.

#### Ring-opening reactions of thiiranes **1a** and **1b** with PhSH **2e** or HOCH<sub>2</sub>CH<sub>2</sub>SH **2f**

The reaction of **1a** or **1b** with **2e** and **2f** using Na<sup>+</sup>-zeolite X or Et<sub>3</sub>N in MeOH also produced regioselectively **3a,e** and **3a,f** or **3b,e** and **3b,f**, respectively (Table 5). However, the reaction using Na<sup>+</sup>-zeolite X in benzene instead of MeOH did not produce **3** (Table 5). This would be explained by the more difficult formation of the intimate ion-pair (in Scheme 1) in benzene

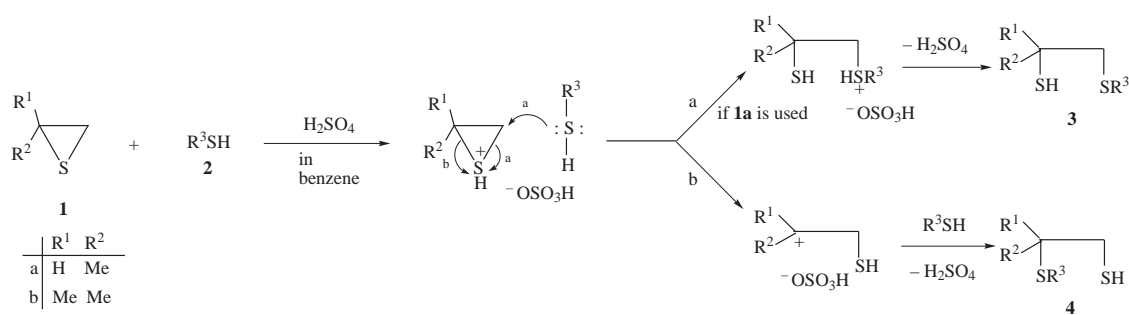
owing to the bulkiness of Ph or HOCH<sub>2</sub>CH<sub>2</sub> in **2e** or **2f**; an intramolecular hydrogen-bond between the thiol proton in **2f** and the oxygen of the HOCH<sub>2</sub>CH<sub>2</sub> group probably causes the bulkiness of **2f**. The reaction using Et<sub>3</sub>N in benzene instead of MeOH gave **3** in low yields (Table 5), nevertheless the use of **2a** or **2b** instead of **2e** or **2f** did not give **3**, as described above. This low production of **3** is probably due to the higher nucleophilicity (described below) of **2e** and **2f** than **2a** and **2b**.

Under the same conditions, the yield of **3** in the reaction of **1a** with **2e** or **2f** was higher than that with **2a** or **2b** (Tables 1 and 5). By-product **5** was not formed in the case of **2e** and **2f** (Table 5) although **5** was formed for the reaction with **2a** and **2b** as described above. This suggests that **2e** and **2f** are more nucleophilic than **2a** and **2b**; a phenyl resonance-effect of **2e** and the

**Table 6** Acid-catalysed ring-opening reactions of thiiranes **1a–c** (4.0 mmol) with thiols **2** using H<sup>+</sup>-zeolite X or H<sub>2</sub>SO<sub>4</sub> at 25 °C for 24 h

| Thiirane  | R of RSH <b>2</b>                                 | <b>2</b> /mmol | Catalyst (180 mg)              | Solvent (8.0 cm <sup>3</sup> ) | Yield <sup>a</sup> (%) <b>3</b> |
|-----------|---|----------------|--------------------------------|--------------------------------|---------------------------------|
| <b>1a</b> | <b>a</b> ; R = Et                                 | 20             | H <sup>+</sup> -zeolite X      | MeOH                           | 0                               |
| <b>1a</b> | <b>a</b> ; R = Et                                 | 20             | H <sub>2</sub> SO <sub>4</sub> | PhH                            | 38                              |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup>                    | 20             | H <sup>+</sup> -zeolite X      | MeOH                           | 0                               |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup>                    | 20             | H <sup>+</sup> -zeolite X      | PhH                            | 0                               |
| <b>1a</b> | <b>b</b> ; R = Bu <sup>n</sup>                    | 20             | H <sub>2</sub> SO <sub>4</sub> | PhH                            | 16                              |
| <b>1a</b> | <b>e</b> ; R = Ph                                 | 4.0            | H <sup>+</sup> -zeolite X      | MeOH                           | 50                              |
| <b>1a</b> | <b>f</b> ; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | H <sup>+</sup> -zeolite X      | MeOH                           | 0                               |
| <b>1a</b> | <b>f</b> ; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | H <sub>2</sub> SO <sub>4</sub> | PhH                            | 52                              |
| <b>1b</b> | <b>a</b> ; R = Et                                 | 20             | H <sup>+</sup> -zeolite X      | MeOH                           | 0                               |
| <b>1b</b> | <b>a</b> ; R = Et                                 | 20             | H <sup>+</sup> -zeolite X      | PhH                            | 0                               |
| <b>1b</b> | <b>a</b> ; R = Et                                 | 20             | H <sub>2</sub> SO <sub>4</sub> | PhH                            | 19 <sup>b</sup>                 |
| <b>1b</b> | <b>b</b> ; R = Bu <sup>n</sup>                    | 20             | H <sup>+</sup> -zeolite X      | MeOH                           | 0                               |
| <b>1b</b> | <b>e</b> ; R = Ph                                 | 4.0            | H <sup>+</sup> -zeolite X      | MeOH                           | 42                              |
| <b>1b</b> | <b>e</b> ; R = Ph                                 | 4.0            | H <sup>+</sup> -zeolite X      | PhH                            | 0                               |
| <b>1b</b> | <b>e</b> ; R = Ph                                 | 4.0            | H <sub>2</sub> SO <sub>4</sub> | PhH                            | 8.7                             |
| <b>1b</b> | <b>f</b> ; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | H <sup>+</sup> -zeolite X      | MeOH                           | 0                               |
| <b>1b</b> | <b>f</b> ; R = CH <sub>2</sub> CH <sub>2</sub> OH | 20             | H <sup>+</sup> -zeolite X      | PhH                            | 0                               |
| <b>1c</b> | <b>a</b> ; R = Et                                 | 4.0            | H <sup>+</sup> -zeolite X      | MeOH                           | 0 <sup>c</sup>                  |
| <b>1c</b> | <b>a</b> ; R = Et                                 | 4.0            | H <sup>+</sup> -zeolite X      | PhH                            | 0 <sup>c</sup>                  |

<sup>a</sup> The yields are based on the amount of **1** used. <sup>b</sup> Compound **4b,a** was formed in 20% yield besides **3b,a**. <sup>c</sup> Product **4c,a** was not formed.

**Scheme 3**

intramolecular hydrogen-bonding of **2f** might enhance their nucleophilicities. The reactivity of **2e** and **2f** towards **1b** must be lower than towards **1a** owing to the steric effect caused by both the two methyl groups in **1b** and the bulkiness of **2e** and **2f**. Thus, under the same conditions, the yield of **3** in the reaction of **1b** with **2e** or **2f** may be lower than that in the reaction of **1a** with **2e** or **2f** (Table 5).

The yield of **3** in the non-catalytic reaction of **1a** with **2e** or **2f** in MeOH was much lower than that in the catalytic reaction, but the reaction of **1b** with **2e** or **2f** in MeOH was almost insensitive to the presence of catalysts (Table 5). Since the reaction between the bulky compounds such as **1b** and **2e** or **2f** is sterically controlled, the reactivity might not be affected by the presence of catalysts; the catalyst can only enhance the nucleophilicity of **2** via electronic effects, as seen in Schemes 1 and 2, and thus would not affect a sterically controlled reaction.

#### Acid-catalysed ring-opening reactions

The reactions of **1a–c** were not catalysed by H<sup>+</sup>-zeolite X in MeOH or benzene, except the reactions with very reactive **2e** in MeOH, while the reactions of **1a** and **1b** were catalysed by H<sub>2</sub>SO<sub>4</sub> in benzene (Table 6). Although the S-atom is a soft base, which is more difficult to protonate, the protonation of **1** may occur prior to ring-opening in the presence of the strongly acidic H<sub>2</sub>SO<sub>4</sub>. A cationic intermediate in the reaction (path a in Scheme 3) catalysed by H<sub>2</sub>SO<sub>4</sub> can be stabilised in benzene as an intimate ion-pair with <sup>-</sup>OSO<sub>3</sub>H, giving **3**; **4** would be formed via an S<sub>N</sub>1 reaction (path b in Scheme 3) between a stable tertiary carbocation formed from **1b** and the less nucleophilic **2a**.

If the ring-opening of **1** occurred after protonation at the S-atom using H<sup>+</sup>-zeolite X, a cationic intermediate formed in the ring-opening should be stabilised. However, the inter-

mediate could not be stabilised by solvation in MeOH or as the intimate ion-pair in benzene unlike the zwitterion in Scheme 1 probably because the counter-anion is highly dissipated in the zeolite lattice.

#### Experimental

IR spectra were obtained on a Hitachi EPI-G3 spectrometer. <sup>1</sup>H NMR spectra were taken with a Nippondenshi PMX-60SI instrument (*J* values are given in Hz). GLC-MS were recorded with a Shimadzu QP-5000 spectrometer linked to a Shimadzu GC-17A; the column (15 m × 0.25 mm) coated with DB-1 (0.25 μm film) is made by J & W Scientific. GLC was performed with a Shimadzu GC-8A using a glass column (1 m × 3 mm) packed with 10% SE-30 on 60–80 mesh Chromosorb W (AW-DMCS). Two runs agreed to within 3% error for the yields of the products which were determined by replicate GLC analyses.

MeOH, EtOH, *n*-PrOH, *n*-BuOH, EtOEt, CH<sub>2</sub>Cl<sub>2</sub> and PhH were purified by standard methods before use. The following compounds were reagent grade (Nacalai Tesque), and were used without further purification: H<sub>2</sub>SO<sub>4</sub>, Et<sub>3</sub>N, 2-methylthiirane **1a**, 2,2-dimethylthiirane **1b**, ethanethiol **2a**, butanethiol **2b**, 2-methylpropane-1-thiol **2c**, 2-methylpropane-2-thiol **2d**, phenylthiol **2e** and 2-mercaptoethan-1-ol **2f**. 2-Phenylthiirane **1c** was synthesized by the literature method.<sup>16</sup>

Na<sup>+</sup>-zeolite X and Na<sup>+</sup>-zeolite A-3 were Tōyōsōda synthetic powdery Na<sup>+</sup>-zeolite F-9 (*i.e.* X) and A-3 which have minimum pore diameters of 10 and 3 Å, respectively. H<sup>+</sup>-zeolite X was prepared by the calcination (350 °C, 1 h) of NH<sub>4</sub><sup>+</sup>-exchanged zeolites formed from Na<sup>+</sup>-zeolite X; 8 g of Na<sup>+</sup>-zeolite X were treated three times with 200 cm<sup>3</sup> of aqueous NH<sub>4</sub>Cl (0.5 mol dm<sup>-3</sup>), washed with 500 cm<sup>3</sup> water, dried in air and calcined. The zeolites were dehydrated at 190 °C for 12 h before use.

**Ring-opening reactions of 2-methyl-, 2,2-dimethyl- and 2-phenylthiiranes 1a–c with alkylthiols 2a–d using Na<sup>+</sup>-zeolite X, Na<sup>+</sup>-zeolite A-3, H<sup>+</sup>-zeolite X, Et<sub>3</sub>N or H<sub>2</sub>SO<sub>4</sub>**

The ring-opening reactions of thiiranes **1a–c** (4.0 mmol) with thiols **2a–d** were carried out in the presence or absence of catalyst under the conditions described in Tables 1–4 and 6. The yields of the products were determined by GLC analysis of the reaction mixture. In reactions using the zeolite catalysts, the GLC analysis was performed after filtration of the catalysts. The products **3–5** were isolated by thin layer chromatography using silica gel (Merk 60F254) after column chromatography employing silica gel (Fujisiriaru Chem. BW-1277ZH), and the structures were confirmed by the spectroscopic data shown below. The elemental analyses for **3a,a–c**, **3b,a**, **3b,b** and **5a,b** could not give satisfactory results because these compounds are volatile at room temperature. The products **3a,a–c** and **5a,b** or **3b,a** and **3b,b** have a doublet or singlet thiol proton, respectively, as shown by <sup>1</sup>H NMR. This clearly indicates that these compounds are formed by the attack of **2** or **3** on not the C-2 but the C-3-position of **1**.

**1-(Ethylthio)propane-2-thiol 3a,a.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.25 (3H, t, *J* 7.0, CH<sub>2</sub>Me), 1.38 (3H, d, *J* 6.0, CHMe), 1.97 (1H, d, *J* 5.6, CHSH), 2.57 (2H, q, *J* 7.0, SCH<sub>2</sub>Me), 2.78 (2H, d, *J* 6.0, CHCH<sub>2</sub>S) and 2.8–3.4 (1H, m, CH); *m/z* 136 (M<sup>+</sup>), 103 (M<sup>+</sup> – SH), 76, 75, 74, 73, 64, 61, 48, 47, 45, 41 and 40.

**1-[2-(Ethylthio)-1-methylethyl]thio}propane-2-thiol 5a,a.** *M/z* 210 (M<sup>+</sup>), 176 (M<sup>+</sup> – H<sub>2</sub>S), 138, 136 (M<sup>+</sup> – C<sub>3</sub>H<sub>6</sub>S), 135, 103 (M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>S<sub>2</sub>), 93, 89, 76, 75 (C<sub>3</sub>H<sub>7</sub>S<sup>+</sup>), 74, 73, 64, 61 (C<sub>2</sub>H<sub>5</sub>S<sup>+</sup>), 60, 59, 47, 45, 42, 41 and 40. This compound was not isolated, but the structure was confirmed by the peaks of the GLC-MS which correspond to those of **5a,b**. The yield of **5a,a** was determined by the assumption that it has the same GLC area-sensitivity for weight as **3a,a**; **5a,b** has the same sensitivity as **3a,b**.

**1-(Butylthio)propane-2-thiol 3a,b.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 0.90 (3H, t, *J* 6.0, MeCH<sub>2</sub>), 1.10–1.90 (4H, m, MeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.95 (1H, d, *J* 6.0, CHSH), 2.52 (2H, t, *J* 6.0, SCH<sub>2</sub>CH<sub>2</sub>), 2.68 (2H, d, *J* 6.0, SCH<sub>2</sub>CH) and 2.70–3.33 (1H, m, CH); *m/z* 164 (M<sup>+</sup>), 131 (M<sup>+</sup> – SH), 104, 103, 89, 75, 74, 61, 57, 56, 55, 47, 45 and 41.

**1-[2-(Butylthio)-1-methylethyl]thio}propane-2-thiol 5a,b.** Liquid,  $\delta_{\text{H}}$  (PhH) 0.90 (3H, t, *J* 6.0, MeCH<sub>2</sub>), 1.39 (3H, d, *J* 6.0, MeCHSH or MeCHS), 1.42 (3H, d, *J* 6.0, MeCHS or MeCHSH), 1.10–1.90 (4H, m, MeCH<sub>2</sub>CH<sub>2</sub>), 1.99 (1H, d, *J* 3.0, CHSH), 2.52 (2H, t, *J* 6.0, CH<sub>2</sub>CH<sub>2</sub>S), 2.78 (4H, d, *J* 6.0, SCH<sub>2</sub>CHS and SCH<sub>2</sub>CHSH) and 2.27–3.37 (2H, m, CHSH and CHS); *m/z* 238 (M<sup>+</sup>), 204 (M<sup>+</sup> – H<sub>2</sub>S), 166, 164 (M<sup>+</sup> – C<sub>3</sub>H<sub>6</sub>S), 163, 131 (M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>S<sub>2</sub>), 89, 75 (C<sub>3</sub>H<sub>7</sub>S<sup>+</sup>), 74, 73, 64, 61 (C<sub>2</sub>H<sub>5</sub>S<sup>+</sup>), 59, 57, 55, 47, 45 and 41.

**1-(sec-Butylthio)propane-2-thiol 3a,c.** Liquid,  $\delta_{\text{H}}$  (PhH) 0.97 (3H, t, *J* 6.0, MeCH<sub>2</sub>), 1.10–1.90 (2H, m, MeCH<sub>2</sub>CH), 1.25 (3H, d, *J* 6.0, MeCHS or MeCHSH), 1.38 (3H, d, *J* 6.0, MeCHS or MeCHSH), 1.98 (1H, d, *J* 6.0, SH), 2.70 (2H, d, *J* 6.0, CHCH<sub>2</sub>S) and 2.33–3.33 (2H, m, MeCHS and MeCHSH); *m/z* 164 (M<sup>+</sup>), 131 (M<sup>+</sup> – SH), 117, 108, 75, 74, 73, 64, 61, 60, 59, 58, 57, 56, 55, 47, 45, 42, 41 and 40.

**1-[2-(sec-Butylthio)-1-methylethyl]thio}propane-2-thiol 5a,c.** *M/z* 238 (M<sup>+</sup>), 204 (M<sup>+</sup> – H<sub>2</sub>S), 180 (M<sup>+</sup> – BuH), 164 (M<sup>+</sup> – C<sub>3</sub>H<sub>6</sub>S), 138, 135, 131 (M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>S<sub>2</sub>), 119, 115, 108, 106, 75 (C<sub>3</sub>H<sub>7</sub>S<sup>+</sup>), 74, 73, 64, 61 (C<sub>2</sub>H<sub>5</sub>S<sup>+</sup>), 60, 59, 58, 57 (C<sub>4</sub>H<sub>9</sub><sup>+</sup>), 56, 55, 47, 46, 45, 42, 41 and 40. Although this compound was not isolated, the structure and the yield were determined by a similar method to that described for **5a,a**.

**2-(tert-Butylthio)propane-2-thiol 3a,d.** *M/z* 164 (M<sup>+</sup>), 131 (M<sup>+</sup> – SH), 117, 108, 75, 74, 61, 60, 59, 58, 57, 47, 45, 41 and 40. The relative intensity to *m/z* 164 (M<sup>+</sup>) of *m/z* 57 (tert-Bu<sup>+</sup>) was higher than that of *m/z* 57 (sec-Bu<sup>+</sup>) for **3a,c**. This compound was not isolated, but the structure was confirmed by the above GLC-MS. The yield was determined by the assumption that **3a,c** and **3a,d** have the same area-sensitivity for GLC analysis.

**1-(Ethylthio)-2-methylpropane-2-thiol 3b,a.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.27 (3H, t, *J* 7.0, MeCH<sub>2</sub>), 1.44 (6H, s, MeCMe), 2.20 (1H, s, SH), 2.63 (2H, q, *J* 7.0, MeCH<sub>2</sub>) and 2.80 (2H, s, SCH<sub>2</sub>C); *m/z* 150 (M<sup>+</sup>), 117 (M<sup>+</sup> – SH), 116 (M<sup>+</sup> – H<sub>2</sub>S), 87, 76, 75, 64, 61, 59, 55, 47, 45, 41 and 40.

**2-(Ethylthio)-2-methylpropane-1-thiol 4b,a.** *M/z* 150 (M<sup>+</sup>), 148 (M<sup>+</sup> – H<sub>2</sub>), 116 (M<sup>+</sup> – H<sub>2</sub>S), 103 (M<sup>+</sup> – CH<sub>2</sub>SH), 87, 75, 64, 61, 60, 59, 56, 55, 54, 53, 48, 47, 46, 45, 43 and 41. The peaks of *m/z* 148 and 103 were characteristic for the structure of **4b,a**, not **3b,a**. The fact that the GLC-peak for **4b,a** has a longer retention-time than that of **3b,a** suggests that the SH group of **4b,a** is less shielded by the two methyl groups than the SH group of **3b,a**. The yield of **4b,a** was determined by the assumption that the GLC area-sensitivities for **3b,a** and **4b,a** are the same.

**1-(Butylthio)-2-methylpropane-2-thiol 3b,b.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 0.90 (3H, t, *J* 6.0, MeCH<sub>2</sub>), 1.42 (6H, s, MeCMe), 1.05–1.90 (4H, m, MeCH<sub>2</sub>CH<sub>2</sub>), 2.17 (1H, s, SH), 2.57 (2H, t, *J* 6.0, SCH<sub>2</sub>CH<sub>2</sub>) and 2.76 (2H, s, SCH<sub>2</sub>C); *m/z* 178 (M<sup>+</sup>), 176 (M<sup>+</sup> – H<sub>2</sub>), 144 (M<sup>+</sup> – H<sub>2</sub>S), 133, 104, 101, 89, 88, 87, 75, 64, 61, 60, 59, 57, 56, 55, 54, 53, 48, 47, 45, 41 and 40.

**1-(Ethylthio)-2-phenylethane-2-thiol 3c,a.**  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.20 (3H, t, *J* 7.2, Me), 1.56 (1H, d, *J* 7.2, CHSH), 2.46 (2H, q, *J* 7.2, CH<sub>2</sub>Me), 3.05 (2H, t, *J* 7.2, SCH<sub>2</sub>CH), 4.05 (1H, q, *J* 7.2, CH<sub>2</sub>CHSH) and 7.07–7.60 (5H, m, phenyl H); *m/z* 198 (M<sup>+</sup>), 165 (M<sup>+</sup> – SH), 151, 135, 123 (M<sup>+</sup> – CH<sub>2</sub>SEt), 122, 104, 103, 91, 78, 77, 76, 75, 59, 51, 47 and 45. The relative intensity to *m/z* 198 (M<sup>+</sup>) of *m/z* 123 was much higher than that of **4c,a**, supporting this structure.

**2-(Ethylthio)-2-phenylethane-1-thiol 4c,a.**  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.17 (3H, t, *J* 7.2, Me), 1.47 (1H, t, *J* 7.2, CH<sub>2</sub>SH), 2.38 (2H, q, *J* 7.2, CH<sub>2</sub>Me), 2.95 (2H, t, *J* 7.2, CHCH<sub>2</sub>SH), 3.92 (1H, t, *J* 7.2, CH<sub>2</sub>CHS) and 7.07–7.60 (5H, m, phenyl H); *m/z* 198 (M<sup>+</sup>), 151 (M<sup>+</sup> – CH<sub>2</sub>SH), 137, 135, 123, 104, 103, 91, 78, 77, 59, 51 and 45. The relative intensity to *m/z* 198 (M<sup>+</sup>) of *m/z* 151 was much higher than that of **3c,a**, supporting the structure of **4c,a**.

The products **3c,a** and **4c,a** were separated as a mixture, and the structures were confirmed as indicated above. Their yields were determined by the assumption that these have the same GLC area-sensitivity. The elemental analysis for the mixture was satisfactory (Found: C, 60.48; H, 6.92. Calc. for C<sub>10</sub>H<sub>14</sub>S<sub>2</sub>: C, 60.59; H, 7.12%).

**Ring-opening reactions of 2-methyl- and 2,2-dimethylthiiranes 1a and 1b with PhSH 2e and HOCH<sub>2</sub>CH<sub>2</sub>SH 2f using Na<sup>+</sup>-zeolite X, H<sup>+</sup>-zeolite X, Et<sub>3</sub>N or H<sub>2</sub>SO<sub>4</sub>**

The reactions of **1a** and **1b** with **2e** and **2f** were performed under the conditions described in Tables 5 and 6. Isolation of the products **3a,e**, **3a,f**, **3b,e** and **3b,f** and the determination of their yields were carried out as shown above. The characterisations of the products are given below. The doublet or singlet thiol proton appears in the <sup>1</sup>H NMR spectra of **3a,f** or **3b,e** and **3b,f**, respectively. This supports these compounds being those formed by the attack of **2** on the C-3-position of **1**.

**1-(Phenylthio)propane-2-thiol 3a,e.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.13–

1.67 (3H, m, Me), 1.83–2.00 (1H, m, SH), 2.80–3.30 (3H, m, SCH<sub>2</sub>CH) and 7.00–7.73 (5H, m, phenyl H); *m/z* 184 (M<sup>+</sup>), 123 (PhSCH<sub>2</sub><sup>+</sup>), 110 (PhSH<sup>+</sup>), 109 (PhS<sup>+</sup>), 78, 77, 75 (M<sup>+</sup> – PhS), 74, 69, 66, 65, 61 (M<sup>+</sup> – CH<sub>2</sub>SPh), 59, 51, 50, 47, 46, 45, 44, 42 and 41 (Found: C, 58.68; H, 6.55. Calc. for C<sub>9</sub>H<sub>12</sub>S<sub>2</sub>: C, 58.65; H, 6.56%). If this compound was **4a,e**, the peak *m/z* 137 (M<sup>+</sup> – CH<sub>2</sub>SH) should appear more strongly than the *m/z* 61 peak given above. However, the former peak was scarcely observed. This observation suggests that this product is not **4a,e** but is **3a,e**. The above NMR spectra show multiplet signals for the methyl, SH and methylene. These spectral data do not mean that this product is a mixture of **3a,e** and **4a,e**, but show that **3a,e** with the bulky phenyl group and asymmetric carbon exists as a mixture of conformational isomers.

**2-[(2-Mercaptopropyl)thio]ethan-1-ol 3a.f.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.37 (3H, d, *J* 6.4, MeCH), 0.98 (1H, d, *J* 6.0, CHSH), 2.73 (2H, t, *J* 6.0, SCH<sub>2</sub>CH<sub>2</sub>), 2.75 (2H, d, *J* 6.0, CHCH<sub>2</sub>), 2.80–3.40 (2H, m, OH and CH) and 3.73 (2H, t, *J* 6.0, OCH<sub>2</sub>); *m/z* 152 (M<sup>+</sup>), 134 (M<sup>+</sup> – H<sub>2</sub>O), 119 (M<sup>+</sup> – HS), 108, 101, 92, 91, 75, 74, 73, 62, 61, 59, 47, 46, 45 and 41. Elemental analysis was not satisfactory because of a minor impurity.

**2-Methyl-1-(phenylthio)propane-2-thiol 3b.e.** Liquid,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.44 (6H, s, MeCMe), 2.19 (1H, s, SH), 3.23 (2H, s, SCH<sub>2</sub>) and 7.13–7.73 (5H, m, phenyl H); *m/z* 198 (M<sup>+</sup>), 165 (M<sup>+</sup> – HS), 164 (M<sup>+</sup> – H<sub>2</sub>S), 142, 141, 124, 123, 122, 110, 109, 91, 89, 78, 77, 75, 69, 65, 59, 55, 51, 50, 47, 45 and 41. Elemental analysis was also not satisfactory due to a minor impurity.

**2-[(2-Mercapto-2-methylpropyl)thio]ethan-1-ol 3b.f.** Liquid,  $\nu_{\text{max}}$ (neat)/cm<sup>-1</sup> 3360 (OH), 2960, 2920, 2870, 2540 (SH), 1460, 1385, 1370, 1272, 1208, 1135, 1055 and 1020;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.43 (6H, s, MeCMe), 2.16 (1H, s, SH), 2.17–2.67 (1H, br, OH), 2.80 (2H, t, *J* 6.0, SCH<sub>2</sub>CH<sub>2</sub>), 2.82 (2H, s, SCH<sub>2</sub>C) and 3.75 (2H, t, *J* 6.0, OCH<sub>2</sub>); *m/z* 166 (M<sup>+</sup>), 148 (M<sup>+</sup> – H<sub>2</sub>O), 133 (M<sup>+</sup> – HS), 122, 115, 101, 92, 89, 87, 75, 74, 61, 59, 55, 47, 45 and 41 (Found: C, 43.55; H, 8.36. Calc. for C<sub>6</sub>H<sub>14</sub>OS<sub>2</sub>: C, 43.33; H, 8.49%).

#### The relative reactivity of thiiranes **1a–c** with EtSH **2a**

A mixture of **1a** (2.0 mmol), **1b** (2.0 mmol) and **2a** (10.0 mmol) was dissolved in MeOH (4.0 cm<sup>3</sup>) in the presence of Na<sup>+</sup>-zeolite X (90 mg), and allowed to react at 25 °C for 24 h. The reaction

mixture was treated as described above, and we obtained **3a,a** (35%) and **3b,a** (45%) by GLC analysis. A similar reaction of **1a** (2.0 mmol) and **1c** (2.0 mmol) with **2a** (10.0 mmol) in MeOH (4.0 cm<sup>3</sup>) in the presence of Na<sup>+</sup>-zeolite X (90 mg) at 25 °C for 24 h gave **3a,a** (45%) and a mixture (39%) of **3c,a** and **4c,a**. Thus, the relative reactivity (giving **3** or the mixture of **3** and **4**) of thiiranes **1a–c** with **2a** is **1b** > **1a** > **1c**. The products **3a,a**, **3b,a**, **3c,a** and **4c,a** were stable under the reaction conditions using Na<sup>+</sup>-zeolite X in MeOH. Thus, the yields of the products may reflect the reactivity.

#### References

- 1 H. van Bekkum and H. W. Kouwenhoven, *Recl. Trav. Chim. Pays-Bas*, 1989, **108**, 283.
- 2 K. Smith, *Bull. Soc. Chim. Fr.*, 1989, 272.
- 3 M. Onaka and Y. Izumi, *Yūkiōseikagaku*, 1989, **47**, 233.
- 4 W. Hölderich, M. Hesse and F. Näumann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 226; W. Hölderich, *Stud. Surf. Sci. Catal.*, 1989, **46**, 193.
- 5 M. E. Davis, *Acc. Chem. Res.*, 1993, **26**, 111.
- 6 W. M. H. Sachtler, *Acc. Chem. Res.*, 1993, **26**, 383.
- 7 S. L. Suib, *Chem. Rev.*, 1993, **93**, 803.
- 8 R. Joseph, A. Sudalai and T. Ravindranathan, *Tetrahedron Lett.*, 1994, **35**, 5493.
- 9 M. V. R. Reddy, S. V. Pitre, I. Bhattacharya and Y. D. Vankar, *Synlett*, 1996, 241.
- 10 A. Gupta, A. Haque and Y. D. Vankar, *Chem. Commun.*, 1996, 1653.
- 11 C. C. J. Culvenor, W. Davies and N. S. Heath, *J. Chem. Soc.*, 1949, 282.
- 12 H. R. Snyder, J. M. Stewart and J. B. Ziegler, *J. Am. Chem. Soc.*, 1947, **69**, 2675.
- 13 H. R. Snyder and J. M. Stewart, US Patents, 1949, 2 490 984 and 2 490 985; *Chem. Abstr.*, 1950, **44**, 2550.
- 14 M. Sander, *Chem. Rev.*, 1966, **66**, 297.
- 15 H. R. Snyder and J. M. Stewart, US Patents, 1950, 2 497 100; *Chem. Abstr.*, 1950, **44**, 4025.
- 16 J. M. Stewart, *J. Org. Chem.*, 1963, **28**, 596.
- 17 H. Takeuchi, K. Kitajima, Y. Yamamoto and K. Mizuno, *Chem. Express*, 1992, **7**, 613.
- 18 H. Takeuchi, K. Kitajima, H. Kishioka, K. Kita and K. Koyama, *Chem. Express*, 1993, **8**, 45.
- 19 H. Takeuchi, K. Kitajima, Y. Yamamoto and K. Mizuno, *J. Chem. Soc., Perkin Trans. 2*, 1993, 199.
- 20 H. Takeuchi, H. Kishioka and K. Kitajima, *J. Phys. Org. Chem.*, 1995, **8**, 121.

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