

## A Facile Synthesis of $\alpha,\beta$ -Unsaturated Epoxides via Allyldi-isobutyltelluronium Bromide†

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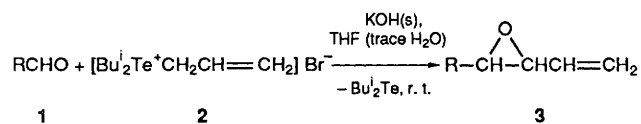
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In the presence of solid KOH, allyldi-isobutyltelluronium bromide **2** reacts directly with aromatic aldehydes at room temperature under solid-liquid phase-transfer conditions to afford  $\alpha,\beta$ -unsaturated epoxides **3** in excellent yields.

$\alpha,\beta$ -Unsaturated epoxides are important synthetic intermediates for synthesis of natural products.<sup>1</sup> However, they cannot be prepared by conventional methods from allylic dimethylsulphonium ylides, which undergo [2,3] sigmatropic rearrangement,<sup>2</sup> nor from allylic diphenyl sulphonium ylides, which are difficult to prepare.<sup>3</sup> Recently, Mioskowski *et al.* described the synthesis of  $\alpha,\beta$ -unsaturated epoxides via allylic arsonium ylide<sup>4</sup> and allylic telluronium ylide<sup>5</sup> respectively, both procedures, however, suffer from strict reaction conditions and rather troublesome workup.

Recently we reported that arsonium salts react with aldehydes in the presence of potassium carbonate to achieve the alkenation under phase-transfer conditions, and the

application of this to the synthesis of certain natural products.<sup>6</sup> To our knowledge, no application of phase-transfer techniques in telluronium ylide is described in the literature. In this communication, we report that  $\alpha,\beta$ -unsaturated epoxides can be directly synthesized from aromatic aldehydes at room



|                                                          |                                                                         |
|----------------------------------------------------------|-------------------------------------------------------------------------|
| <b>a</b> ; R = C <sub>6</sub> H <sub>5</sub>             | <b>g</b> ; R = 1-naphthyl                                               |
| <b>b</b> ; R = <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> | <b>h</b> ; R = 2-naphthyl                                               |
| <b>c</b> ; R = <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> | <b>i</b> ; R = 2-pyridyl                                                |
| <b>d</b> ; R = <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> | <b>j</b> ; R = 3-pyridyl                                                |
| <b>e</b> ; R = <i>p</i> -FC <sub>6</sub> H <sub>4</sub>  | <b>k</b> ; R = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> |
| <b>f</b> ; R = 4-biphenyl                                |                                                                         |

† This paper is the 88th report on the synthetic application of elemento-organic compounds of 15th and 16th groups.

**Table 1** Synthesis of  $\alpha,\beta$ -unsaturated epoxides **3** via telluronium salt **2**<sup>a</sup>

| Compound<br><b>3</b> | R                                                        | Reaction<br>time/h | Yield (%) | <i>cis</i> : <i>trans</i> <sup>b</sup> |
|----------------------|----------------------------------------------------------|--------------------|-----------|----------------------------------------|
| <b>a</b>             | C <sub>6</sub> H <sub>5</sub>                            | 8                  | 96        | 70 : 30                                |
| <b>b</b>             | <i>p</i> -BrC <sub>6</sub> H <sub>4</sub>                | 5                  | 96        | 71 : 29                                |
| <b>c</b>             | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>                | 6.5                | 94        | 60 : 40                                |
| <b>d</b>             | <i>m</i> -ClC <sub>6</sub> H <sub>4</sub>                | 7                  | 99        | 65 : 35                                |
| <b>e</b>             | <i>p</i> -FC <sub>6</sub> H <sub>4</sub>                 | 5                  | 88        | 68 : 32                                |
| <b>f</b>             | 4-Biphenyl                                               | 4.5                | 99        | 77 : 23                                |
| <b>g</b>             | 1-Naphthyl                                               | 5                  | 97        | 69 : 31                                |
| <b>h</b>             | 2-Naphthyl                                               | 4.5                | 97        | 71 : 29                                |
| <b>i</b>             | 2-Pyridyl                                                | 5                  | 85        | 64 : 36                                |
| <b>j</b>             | 3-Pyridyl                                                | 4                  | 85        | 55 : 45                                |
| <b>k</b>             | <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 30                 | 73        | 70 : 30                                |

<sup>a</sup> All the products were characterized by <sup>1</sup>H NMR, MS, and IR; <sup>b</sup> The ratio of the isomers is estimated both by capillary GC and <sup>1</sup>H NMR; the products predominating in *cis* forms are in agreement with that reported by Osuka and Suzuki.<sup>5</sup>

temp. in excellent yields by treating with allyldi-isobutyltelluronium bromide **2**<sup>‡</sup> using solid potassium hydroxide as a base under phase-transfer conditions.

It is noteworthy that weak bases such as triethylamine, piperidine, potassium carbonate and alumina-supported potassium carbonate did not evoke the reaction at room temp. even after 50–60 h, although when alumina-supported potassium fluoride and caesium carbonate were used,  $\alpha,\beta$ -unsaturated epoxides were synthesized after a long reaction time at room temp. Tetrahydrofuran (THF) is the best solvent for the reaction. § Nevertheless in dimethylformamide (DMF) and

<sup>‡</sup> This salt was easily obtained by the reaction of di-isobutyl telluride and allyl bromide without solvent at room temp. for 4 h in 87% yield, m.p. 94–95 °C (lit.,<sup>5</sup> 94.5–95.5 °C).

§ Allyldi-isobutyltelluronium bromide **2** (2.0 mmol), aldehyde **1** (1.0 mmol), KOH(s) (2.0 mmol), and 4 ml THF (10  $\mu$ l H<sub>2</sub>O) were mixed in a reaction tube under N<sub>2</sub>, and stirred at room temperature. After the reaction was completed (monitored by TLC), the resulting mixture was filtered to remove the inorganic salt. Flash chromatography gave the pure product.

dimethyl sulphoxide (DMSO), reactions also occur, but a longer time is required and aqueous workup is needed. Fortunately, using a solid-liquid phase-transfer process [KOH(s)/THF (trace H<sub>2</sub>O) system], the desired products **3** were obtained in excellent yields as shown in Table 1.

In summary, the method described herein constitutes a useful and facile synthesis of  $\alpha,\beta$ -unsaturated epoxides with the advantages of a simple procedure, mild reaction conditions and excellent yields.

We are grateful for financial support from the National Natural Science Foundation of China and the Science Foundation of Academia Sinica.

Received, 20th June 1990; Com. 0/02773A

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