

# Efficient Solid-state Reactions of Alcohols: Dehydration, Rearrangement, and Substitution

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Dehydration, rearrangement, and substitution reactions of alcohols occur more efficiently in the solid state than in solution.

During the course of the studies on solid-state organic reactions,<sup>1</sup> the title reactions of alcohols were found to proceed more efficiently in the solid state than in solution. This is of interest as a convenient synthetic method and also from a mechanistic point of view. It is well established that reactions that proceed *via* a carbonium ion intermediate are accelerated in polar solvents. However, our finding shows that the mechanism seems not to be applicable to the reaction in the solid state.

Powdered 1,1-diphenylpropan-1-ol (**1b**) kept in a desiccator filled with HCl gas for 5.5 h gave pure 1,1-diphenylprop-1-ene (**2b**) in 99% yield. By the same method, (**1a**), (**1c**), and (**1d**) gave pure dehydration products, (**2a**), (**2c**), and (**2d**), respectively in almost quantitative yields (Table 1). The dehydration reaction proceeds much faster by using Cl<sub>3</sub>CCO<sub>2</sub>H as a catalyst. For example, a mixture of powdered (**1b**) and an equimolar amount of Cl<sub>3</sub>CCO<sub>2</sub>H was kept at room temperature for 5 min, and the reaction mixture washed with water and dried to give pure (**2b**) in 99% yield. Similarly, (**1a**) and (**1c**) gave (**2a**) and (**2c**), respectively in the yields shown in Table 2. However, the dehydration reaction in benzene gave (**2**) in relatively low yield (Table 2). A solution of (**1b**) (0.5 g) and an equimolar amount of Cl<sub>3</sub>CCO<sub>2</sub>H (0.38 g) kept in benzene (0.5 ml) at room temperature for 5 min followed by work up gave a mixture of (**1b**) and (**2b**) in a ratio of 26 : 74 (<sup>1</sup>H NMR analysis) (Table 2). Similar treatment of (**1c**) gave a mixture of (**1c**) and (**2c**) in a 35 : 65 ratio (Table 2). However, the dehydration in MeOH under the same reaction conditions as above did not occur.

Toluene-*p*-sulphonic acid (TsOH)-catalysed Meyer-Schuster rearrangement<sup>2</sup> of the propargyl alcohol (**3**) also occurred

in the solid state (Table 3). In this case, reaction was carried out by keeping a mixture of powdered (**3**) and an equimolar amount of TsOH at 50 °C for 2–3 h. This reaction is usually carried out by heating (**3**) with conc. H<sub>2</sub>SO<sub>4</sub> in solution. The solid-state reaction is much simpler and proceeds under far milder conditions.

Chlorination of (**5**) to the chloride (**6**) also proceeds efficiently if powdered (**5**) is exposed to HCl gas in a desiccator (Table 4). The same treatment of *t*-butyl alcohol for 30 min gave *t*-butyl chloride in 89% yield. This is a simple and convenient synthetic method for previous *t*-butyl chloride.

The most interesting reaction is the formation of the ether (**8**) from the alcohol (**7**) by treatment with TsOH in the solid state. For example, a mixture of powdered 4-methylbenzhydrol (**7g**) and an equimolar amount of TsOH was kept at room temperature for 10 min, and the reaction mixture was

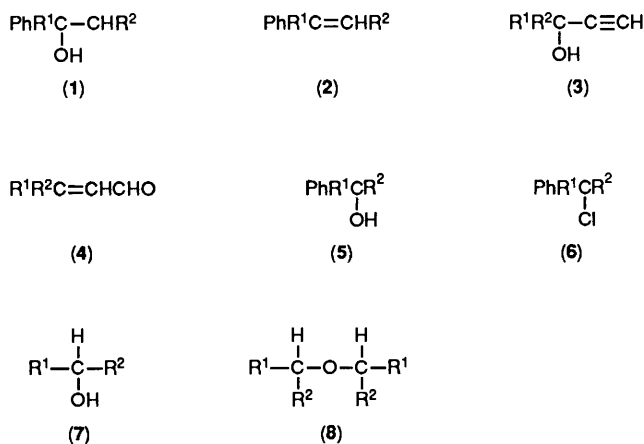


Table 1. HCl-Catalysed dehydration of (**1**) in the solid state.<sup>a</sup>

|     | (1)   |                               | Reaction time/h | Yield/% of ( <b>2</b> ) |
|-----|---|-------------------------------|-----------------|-------------------------|
|     | R <sup>1</sup>  | R <sup>2</sup>                |                 |                         |
| (a) | C <sub>6</sub> H <sub>5</sub> <sup>a</sup>              | H                             | 0.5             | 99                      |
| (b) | C <sub>6</sub> H <sub>5</sub> <sup>b</sup>              | Me                            | 5.5             | 99                      |
| (c) | C <sub>6</sub> H <sub>5</sub> <sup>c</sup>              | C <sub>6</sub> H <sub>5</sub> | 8               | 100                     |
| (d) | <i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> <sup>d</sup> | Me                            | 4               | 97 <sup>b</sup>         |

<sup>a</sup> Reactions were carried out by keeping powdered (**1**) in a desiccator filled with HCl gas at room temperature. <sup>b</sup> A 1 : 1 mixture of the (*E*) and (*Z*) isomers was obtained.

Table 2. Cl<sub>3</sub>CCO<sub>2</sub>H-Catalysed dehydration of (**1**).<sup>a</sup>

| Alcohol       | Yield/% of ( <b>2</b> ) |                 |
|---------------|-------------------------|-----------------|
|               | solid                   | benzene         |
| ( <b>1a</b> ) | 99                      | — <sup>b</sup>  |
| ( <b>1b</b> ) | 99                      | 74 <sup>b</sup> |
| ( <b>1c</b> ) | 97                      | 65 <sup>c</sup> |

<sup>a</sup> All the reactions were carried out at room temperature for 5 min. <sup>b</sup> No reaction occurred. <sup>c</sup> (**1b**) and (**2b**) were obtained in 26 and 74% yields, respectively. <sup>d</sup> (**1c**) and (**2c**) were obtained in 35 and 65% yields, respectively.

Table 3. TsOH-Catalysed Meyer-Schuster rearrangement of (**3**) at 50 °C in the solid state.

|     | (3)  |   | Reaction time/h | Yield/% of ( <b>4</b> ) |
|-----|--|---|-----------------|-------------------------|
|     | R <sup>1</sup>                                     | R <sup>2</sup>  |                 |                         |
| (a) | C <sub>6</sub> H <sub>5</sub>                      | C <sub>6</sub> H <sub>5</sub> <sup>a</sup>                      | 2               | 58                      |
| (b) | C <sub>6</sub> H <sub>5</sub>                      | <i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> <sup>b</sup>         | 3               | 60 <sup>a</sup>         |
| (c) | 2,4-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> | 2,4-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> <sup>c</sup> | 3               | 94                      |

<sup>a</sup> The (*E*) and (*Z*) isomers were obtained in 30 and 70% yields, respectively.

Table 4. Chlorination of (**5**) in the solid state.<sup>a</sup>

|     | (5)  |                               | Reaction time/h | Yield/% of ( <b>6</b> ) |
|-----|--|-------------------------------|-----------------|-------------------------|
|     | R <sup>1</sup>                             | R <sup>2</sup>                |                 |                         |
| (a) | C <sub>6</sub> H <sub>5</sub>              | H                             | 5               | 92                      |
| (b) | C <sub>6</sub> H <sub>5</sub>              | C <sub>6</sub> H <sub>5</sub> | 1.5             | 97                      |
| (c) | <i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> | H                             | 10              | 94                      |

<sup>a</sup> See Table 1 footnote <sup>a</sup>.

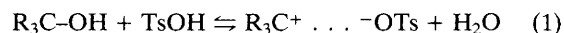
**Table 5.** TsOH-Catalysed etherification of (7) to (8) in the solid state and in solution.<sup>a</sup>

|     | (7)  |  | Reaction conditions |       | Yield/% of (8) |         |      |
|-----|--|--|---------------------|-------|----------------|---------|------|
|     | R <sup>1</sup>                             | R <sup>2</sup>   | Temp./°C            | t/min | solid          | benzene | MeOH |
| (a) | C <sub>6</sub> H <sub>5</sub>              | C <sub>6</sub> H <sub>5</sub>                            | 15                  | 11    | 95             | 45      | 34   |
| (b) | C <sub>6</sub> H <sub>5</sub>              | <i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub>               | 50                  | 120   | 94             | 73      | 37   |
| (c) | C <sub>6</sub> H <sub>5</sub>              | <i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>               | 50                  | 5     | 98             | 53      | 50   |
| (d) | C <sub>6</sub> H <sub>5</sub>              | <i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> | 50                  | 120   | 74             | 58      | 1    |
| (e) | C <sub>6</sub> H <sub>5</sub>              | <i>o</i> -Me-C <sub>6</sub> H <sub>4</sub>               | 50                  | 10    | 96             | 75      | 57   |
| (f) | C <sub>6</sub> H <sub>5</sub>              | <i>m</i> -Me-C <sub>6</sub> H <sub>4</sub>               | 50                  | 30    | 93             | 86      | 89   |
| (g) | C <sub>6</sub> H <sub>5</sub>              | <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>               | 15                  | 10    | 96             | 52      | 10   |
| (h) | <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub> | <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>               | 15                  | 30    | 97             | 59      | 74   |

<sup>a</sup> Reactions were carried out by keeping a mixture of powdered (7) and an equimolar amount of TsOH or by keeping a solution of (7) and an equimolar amount of TsOH in solvent.

extracted with ether. The ether solution was worked up by the usual method and distillation of the crude product gave the corresponding ether (8g) in 96% yield. By the same procedure, other ethers were also synthesized in good yields (Table 5). When the reaction is carried out in benzene or MeOH, the yield is relatively low (Table 5). The synthetic method for (8) in the solid state is much more convenient than the usual one that is carried out by heating (7) with conc. H<sub>2</sub>SO<sub>4</sub> in solution.<sup>3</sup>

When an equimolar mixture of (5) or (7) and TsOH is heated at 47 °C, a yellow colouration is observed, possibly due to carbonium ion formation [equation (1)].<sup>4</sup> Such colouration, which disappears at room temperature, is seen in all the reactions. The reasons for the efficiency of the process in the solid state are not yet known and are under investigation.



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