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# Benzylic Acid Rearrangement in the Solid State

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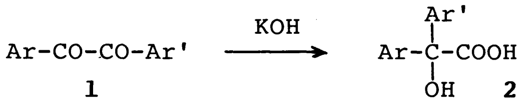
Benzylic acid rearrangements in the solid state were studied and some of them were found to proceed faster than in solution. Although the rearrangement which is initiated by an attack of $OH^-$ and then proceeds via radical intermediate was clarified to be similar to that in solution, the effect of alkali metal hydroxide on the rearrangement in the solid state was different from that in solution.

Benzylic acid rearrangement has long been carried out by heating benzil derivatives and alkali metal hydroxide in aqueous organic solvent. We found that the rearrangement can be carried out without using solvent. We also found that some rearrangements proceed faster in the solid state than in solution. This is very economical and effective synthetic method of benzylic acid.

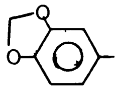
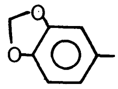
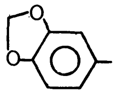
For example, a mixture of finely powdered benzil (**1a**) (0.5 g, 2.38 mmol) and KOH (0.26 g, 4.76 mmol) was heated at 80 °C for 0.2 h, and the reaction product was mixed with 3N HCl (20 ml) to give benzylic acid (**2a**) as colorless needles (0.49 g, 90% yield). Similar treatment of benzil derivatives (**1b-h**) in the solid state also gave the corresponding benzylic acid (**2b-h**) (Table 1). This method is much simpler than the usual one which is carried out by heating benzil and alkali metal hydroxide in aqueous organic solvent.

Although benzils which are substituted with nitro group (**1d** and **1e**) rearranged even at room temperature, those with electron-donating group (**1f-h**) took a long time to complete the rearrangement at 80 °C and **1i** was inert to the reaction (Table 1). This tendency can be interpreted by the reaction pathway which starts by an attack of $HO^-$ to the carbonyl carbon of benzil (Scheme 1). Benzil which is substituted with one chlorine atom (**1b**) rearranged effectively but that with two chlorine atoms (**1c**) did slowly. This result shows that the chlorine atom increases the electron density of the carbonyl carbon of benzil by a resonance and retards the attack of $HO^-$ to the carbonyl carbon.

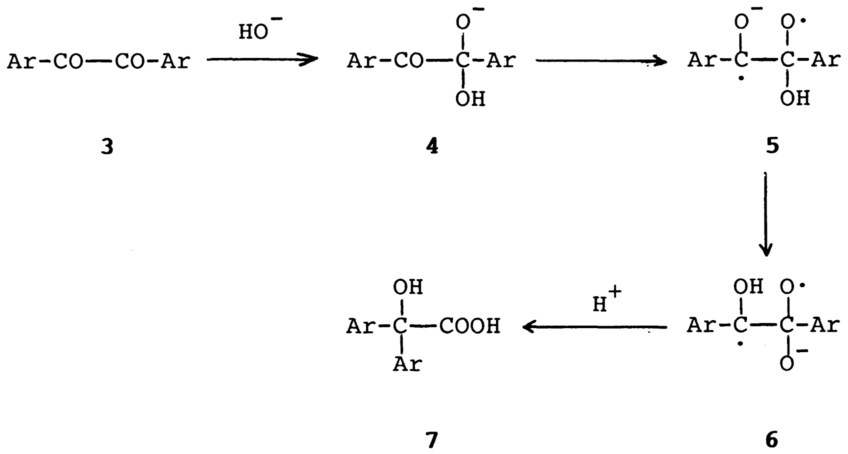


$$\underset{\mathbf{1}}{\text{Ar-CO-CO-Ar'}} \xrightarrow{\text{KOH}} \text{Ar-}\overset{\text{Ar'}}{\underset{\text{OH}}{\text{C}}}\text{-COOH} \quad \mathbf{2}$$

Table 1. Yield of benzylic acid (**2**) produced by treatment of benzil (**1**) with KOH at 80 °C in the solid state

| **1** | Ar | Ar' | Reaction time / h | Yield / % of **2** |
|---|---|---|---|---|
| **a** | $C_6H_5$- | $C_6H_5$- | 0.2 | 90 |
| **b** | $C_6H_5$- | *p*-Cl-$C_6H_4$- | 0.5 | 92 |
| **c** | *p*-Cl-$C_6H_4$- | *p*-Cl-$C_6H_4$- | 6 | 68 |
| **d** | $C_6H_5$- | *p*-$NO_2$-$C_6H_4$- | 0.1[a)] | 93 |
| **e** | *m*-$NO_2$-$C_6H_4$- | *m*-$NO_2$-$C_6H_4$- | 0.1[a)] | 72 |
| **f** | $C_6H_5$- | *p*-MeO-$C_6H_4$- | 6 | 91 |
| **g** | $C_6H_5$- |  | 6 | 95 |
| **h** | *p*-MeO-$C_6H_4$- | *p*-MeO-$C_6H_4$- | 6 | 32 |
| **i** |  |  | 6 | 0 |

a) Carried out at room temperature.



Scheme 1.

Table 2. Effect of alkali metal hydroxide on the benzylic acid rearrangement of **1a** in the solid state and in solution

| Alkali metal hydroxide | Reaction time / h | Yield / % of **2a** Solid state[a)] | Yield / % of **2a** 50% Aqueous EtOH[b)] |
|---|---|---|---|
| LiOH | 6 | 0 | 70 |
| NaOH | 1 | 83 | 91 |
| KOH | 0.2 | 90 | 95 |
| CsOH | 5 | 89 | 43 |
| RbOH | 0.5 | 76 | 52 |
| $Mg(OH)_2$ | 6 | 0 | trace |
| $Ca(OH)_2$ | 6 | 0 | trace |
| $Sr(OH)_2$ | 6 | 0 | 90 |
| $Ba(OH)_2$ | 0.5 | 89 | 70 |
| $Cu(OH)_2$ | 6 | 0 | trace |
| $Al(OH)_3$ | 6 | 0 | trace |

a) Carried out at 80 °C. b) Carried out under reflux for 30 min.

By ESR study, the benzylic acid rearrangement in solution has been proven to proceed via radical intermediate (Scheme 1).[2)] For the benzylic acid rearrangement in the solid state, radical intermediate was also detected. For example, freshly prepared mixture of finely powdered **1e** and

KOH showed a strong ESR signal (g=2.0049) and the signal declined as the reaction proceeded.

Effect of the alkali metal hydroxide on the rate of the benzylic acid rearrangement in the solid state was different from that in solution. The effect on the rate of the rearrangement of **1a** in the solid state increased in the order as follows: KOH>Ba$(OH)_2$>RbOH>NaOH>CsOH (Table 2). On the other hand, the rate of the rearrangement of **1a** in boiling 50% aqueous EtOH and in 67% aqueous dioxane increases in the order: KOH>NaOH>Sr$(OH)_2$>LiOH>Ba$(OH)_2$>RbOH>CsOH (Table 2), and LiOH>NaOH>CsOH>KOH,3) respectively.

The rearrangement by RbOH and Ba$(OH)_2$ proceeded faster in the solid state than in solution (Table 2). However, LiOH and Sr$(OH)_2$ were inert to the rearrangement in the solid state, although these are effective in solution. The reason for the difference is not clear.

## References

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3) W. H. Puterbaugh and W. S. Gaugh, J. Org. Chem., 26, 3513 (1961).

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