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## Pinacol Rearrangement in the Solid State

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The pinacol rearrangement in the solid state was found to proceed faster and more selectively than that in solution. A highly selective rearrangement was observed in the reaction of pinacol in its host-guest complex in the solid state.

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The pinacol rearrangement is usually carried out under drastic conditions such as heating in  $\text{H}_2\text{SO}_4$ . We found that the reaction proceeds faster and more selectively in the solid state. We also found that the migrating group of pinacol depends

on the kind of acid used. Furthermore, a highly selective rearrangement was observed in the solid state reaction of pinacol in the form of a host-guest complex with HCl gas or toluene-*p*-sulphuric acid (*p*-TsOH).

**Table 1.** Pinacol rearrangement catalysed by HCl gas

Pinacol	Reaction conditions		Yield (%) of	
	Temp. (°C)	Time (h)	(2)	(3)
(1a)	80	2.5	48	32
(1b)	20	7.5	63	9
(1c)	20	12.0	71	8
(1d)	25	3.0	90	0
(1e)	70	3.0	85	0
(1f)	50	1.5	85	6

<sup>a</sup> Reaction was carried out by passing dry HCl gas to powdered (1).

**Table 2.** Pinacol rearrangement catalysed by H<sub>2</sub>SO<sub>4</sub> at 112 °C for 2 h

Pinacol	Yield (%) of	
	(2)	(3)
(1a)	56	30
(1b)	64	20
(1c)	78	17
(1d)	80	20
(1e)	88	2
(1f)	74	26

<sup>a</sup> Reaction was carried out by heating a mixture of (1) and 33 wt.% H<sub>2</sub>SO<sub>4</sub> (ca. 1:5 ratio in weight).

**Table 3.** Pinacol rearrangement catalysed by *p*-TsOH at 60 °C

Pinacol	Reaction time (h)	Yield (%) of	
		(2)	(3)
(1a)	2.5	89	8
(1b)	0.5	45	29
(1c)	0.3	70	30
(1d)	0.7	39	19
(1e)	0.7	89	0
(1f)	1.0	54	41

<sup>a</sup> Reaction was carried out by keeping a mixture of 1:3 molar ratio of powdered (1) and *p*-TsOH.

**Table 4.** Pinacol rearrangement catalysed by CCl<sub>3</sub>CO<sub>2</sub>H at 20 °C<sup>a</sup>

Pinacol	Reaction time (h)	Yield (%) of	
		(2)	(3)
(1a)	2.0	21	68
(1b)	3.0	38	62
(1c)	3.0	18	43
(1d)	2.5	38	62
(1e)	1.0	59	30
(1f)	2.0	30	64

<sup>a</sup> Reaction was carried out by keeping a mixture of 1:3 molar ratio of powdered (1a) and CCl<sub>3</sub>CO<sub>2</sub>H.

Passage of dry HCl gas through a flask containing finely powdered (1) at 20–80 °C for the period shown in Table 1 gave the rearranged products (2) and (3) in the yield shown in Table 1. In comparison to the results obtained by carrying out the reaction in 33 wt.% H<sub>2</sub>SO<sub>4</sub> at 112 °C (Table 2), the reaction in the solid state proceeds more effectively under much milder conditions. Selectivity is also high and the 2:3 ratio increases in the former case.

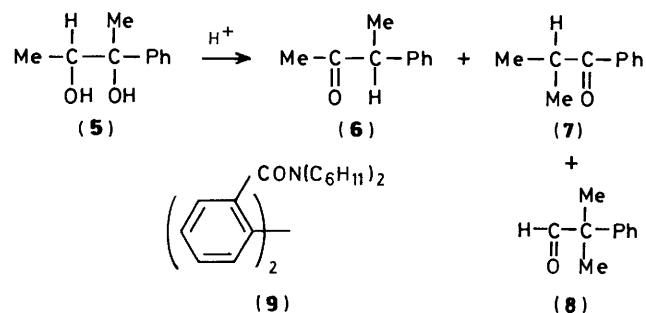
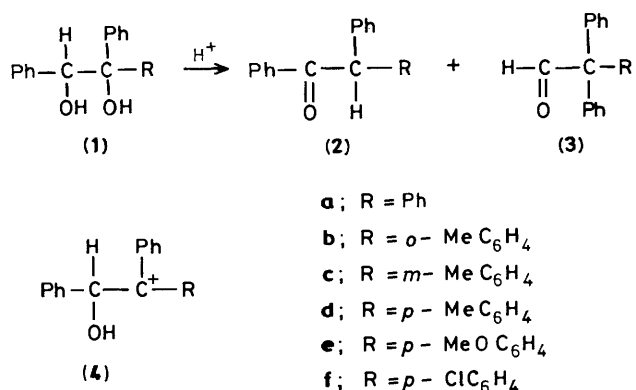
When an organic solid acid is used instead of HCl gas, the rearrangement is accelerated further. When a mixture of 1:3 molar ratio of powdered (1) and *p*-TsOH was kept at 60 °C for the period shown in Table 3, (2) and (3) were obtained in the yields shown in Table 3. This effective reaction is probably due to a more efficient contact of (1) and *p*-TsOH. Similar efficient reactions in the solid state have been reported for host-guest complexation<sup>1</sup> and Baeyer-Villiger oxidation of ketones with *m*-chloroperbenzoic acid.<sup>2</sup>

The hydride migrates more easily than does phenyl anion in (1), and yield of (2) is higher than that of (3) in all reactions shown above. In contrast, a mixture of powdered (1) and CCl<sub>3</sub>CO<sub>2</sub>H when kept at 20 °C for the period shown in Table 4 gave (3) as the major product. However, it is not clear whether

the *pK<sub>a</sub>* values of *p*-TsOH (too strong to measure) and CCl<sub>3</sub>CO<sub>2</sub>H (0.65) (obtained in water) is reflected in their acidity in the solid state and is related to the ratio of (2) and (3). The reaction in the solid state is unaffected by the water produced as evidenced by the fact that continuous removal of the latter under reduced pressure resulted in no obvious effect.

A plausible interpretation of the relation between the kind of acid used and selectivity is as follows. In the carbonium ion (4), initially formed by acid-catalysed dehydroxylation, less bulky hydride migrates more easily to lessen steric crowding and then give the more thermodynamically stable compound (2). The reaction with CCl<sub>3</sub>CO<sub>2</sub>H is faster and, although the reason for this is not clear, it may be controlled kinetically to give (3) as the major product. In the case of (1e), however, (4e) which has greater resonance stabilization because of its MeO substituent, gives mainly the thermodynamically controlled product (2), the reaction of (1e), however, is accelerated because of the greater stability of (4e).

More drastic control of the pinacol rearrangement in the solid state was achieved by using a host-guest complex of pinacol. Treatment of the powdered 1:1 complex of (5) and the host compound (9)<sup>3</sup> with HCl gas at room temperature for 3 h gave (6) in 44% yield as the sole isolable product. This is in contrast to the reaction of (5) with dilute H<sub>2</sub>SO<sub>4</sub> under reflux



(115 °C) which gives (6), (7), and (8) in 48, 29, and 5% yields, respectively. The same selectivity was observed by treating the complex with *p*-TsOH in the solid state. In the host-guest complex, the hydride alone is labile for steric or other reasons.

Reaction in the solid state, especially in the host-guest complex might, therefore, be expected to be useful for efficient reaction control of not only the pinacol rearrangement but also many other organic reactions which have long been carried out in solution.

### References

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