Baeyer–Villiger Reaction in the Solid State

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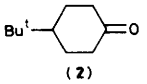
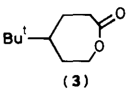
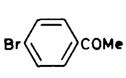
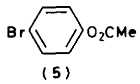
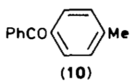
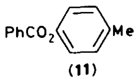
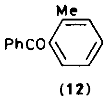
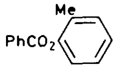
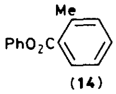
Some Baeyer–Villiger oxidations of ketones with *m*-chloroperbenzoic acid proceed much faster in the solid state than in solution.

Relatively few organic reactions have been carried out in the solid state.[1] We have found that some Baeyer–Villiger oxidations of ketones with *m*-chloroperbenzoic acid (**1**) proceed much faster in the solid state than in solution.

The oxidations were carried out at room temperature with a mixture of powdered ketone and 2 mol. equiv. of powdered peroxy acid (**1**). When the reaction time was longer than 1 day, the reaction mixture was ground once a day with agate pestle

Table 1. Yields of Baeyer–Villiger oxidation products in the solid state and in $CHCl_3$[a].

$$R^1COR^2 \xrightarrow[m\text{-}ClC_6H_4CO_3H\ (\mathbf{1})]{} R^1CO_2R^2$$

Ketone	Reaction time	Product	Yield (%)	
			Solid state	$CHCl_3$[b]
 (**2**)	30 min	 (**3**)	95	94
 (**4**)	5 days	 (**5**)	64	50
$PhCOCH_2Ph$ (**6**)	24 h	$PhCO_2CH_2Ph$ (**7**)	97	46
$PhCOPh$ (**8**)	24 h	$PhCO_2Ph$ (**9**)	85	13
 (**10**)	24 h	 (**11**)	50	12
 (**12**)	4 days	 (**13**) (1:1)  (**14**)	39	6

[a] Molar ratio of ketone and (**1**) is 1 : 2. [b] The reaction was carried out with 1 g of ketone in 50 ml of $CHCl_3$.

and mortar. The excess of peroxy acid (**1**) was decomposed with aqueous 20% $NaHSO_3$, and the product was taken up in ether. The solution was washed with aqueous 20% $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated. The crude product was chromatographed on silica gel (benzene–$CHCl_3$); yields are shown in Table 1. The ratio of (**13**) to (**14**) was determined by ^{1}H n.m.r.

For comparison, the oxidation was also carried out in $CHCl_3$. Yields obtained from a solution of the ketone and 2 molar equiv. of peroxy acid (**1**) in $CHCl_3$ at room temperature are also summarized in Table 1.

In the case of ketones (**2**) and (**4**), there is no marked difference between reactions in the solid state and in $CHCl_3$. However, there is a large difference with the ketones (**6**), (**8**), (**10**), and (**12**) (Table 1). It is surprising that the reaction occurs more easily in the solid state than in solution. Since Baeyer–Villiger reaction in solution usually takes a long time,[2] a reaction which proceeds faster and does not need solvent has many advantages.

We have shown that the movement of molecules in host–guest complex formation in the solid state is easy. Some host–guest complexes can be formed by mixing host and guest compounds in the solid state or by keeping a mixture of powdered host and guest at room temperature.[3] Therefore, the ease of oxidation in the solid state is not unexpected.

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References

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