

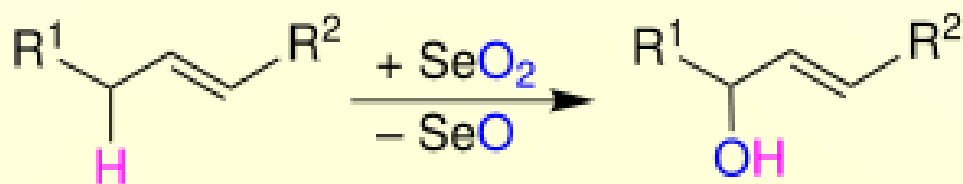
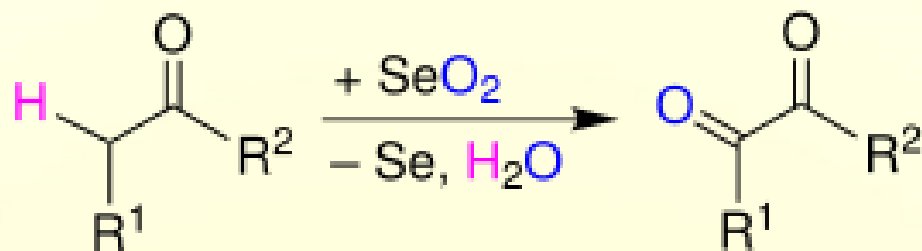
# Riley oxidation

**2017-12-19**

**WZQ**

# Riley oxidation

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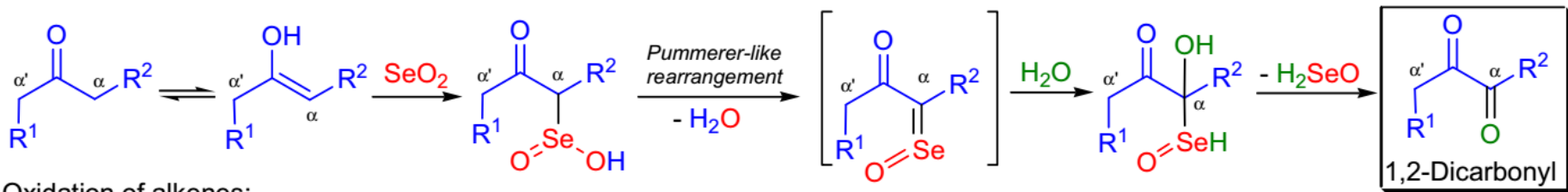


Selenium-dioxide-mediated oxidation of methylene groups to alpha ketones and at the allylic position of olefins is known as **the Riley Oxidation**

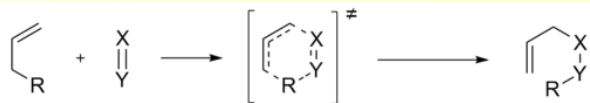
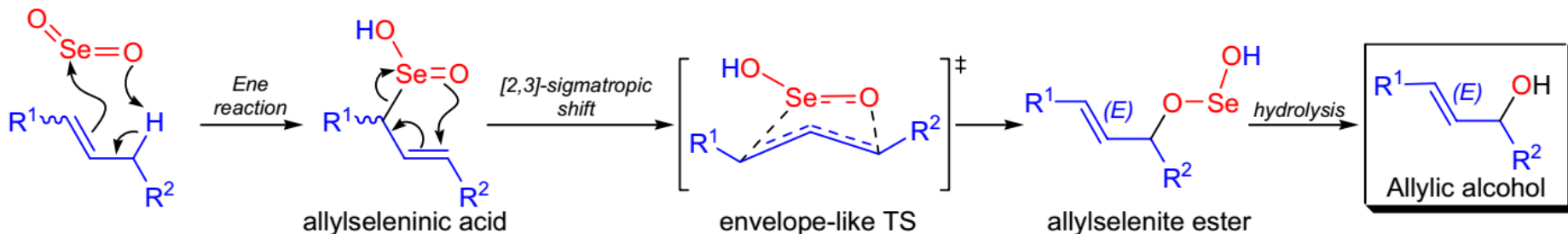
# Riley oxidation

## Mechanism

Oxidation of carbonyl compounds:

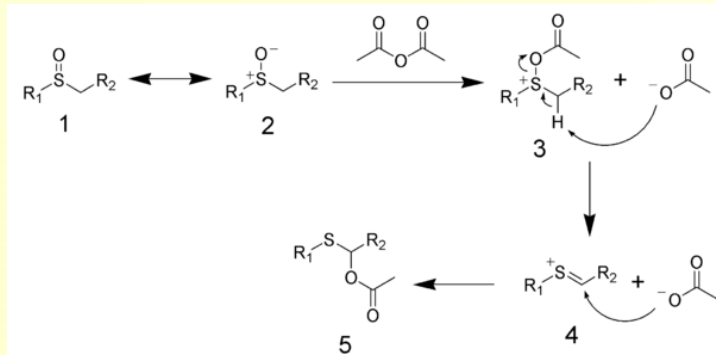


Oxidation of alkenes:



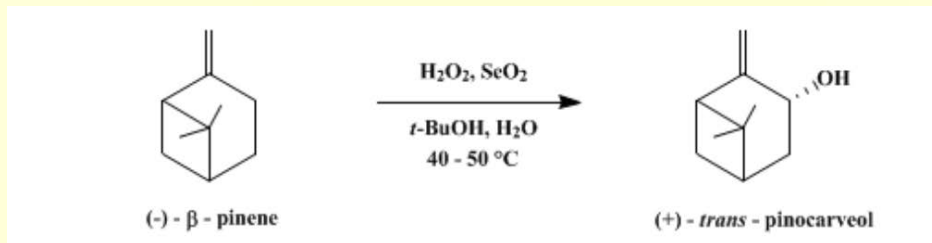
R: H, metal

X=Y: C=C, C≡C, C=O, C=S, C=N, N=N, N=O, etc.

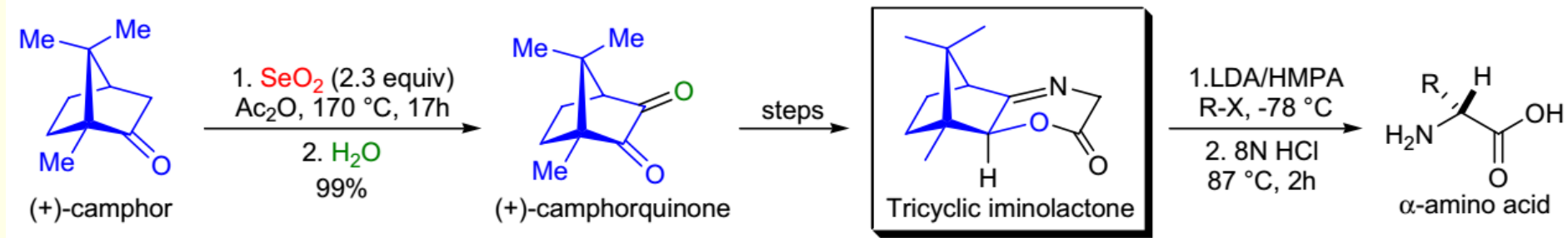
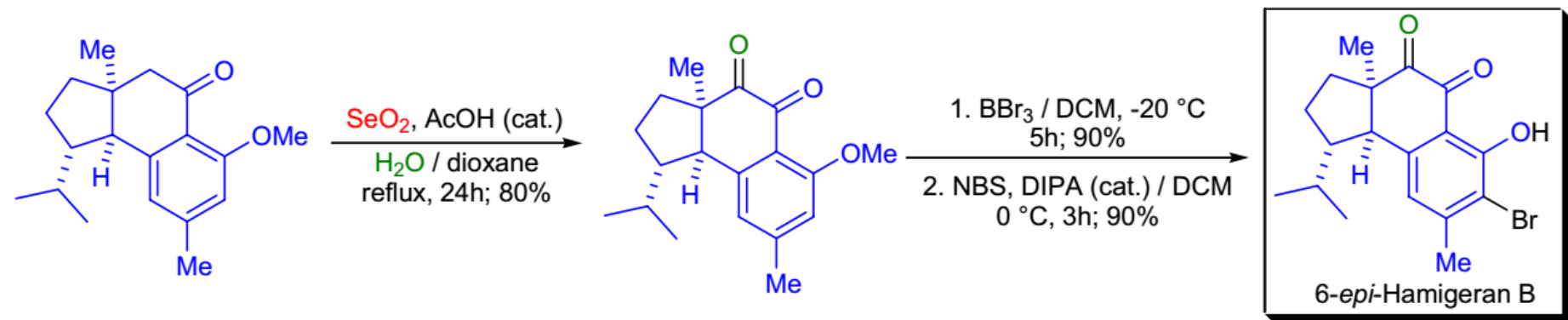


# Riley oxidation

- 1) Ketones and aldehydes with **low molecular weights** are more reactive than the higher homologs;
- 2) Ketones with available  $\alpha$ - and  $\alpha'$ -positions will give rise to a mixture of regioisomers; **the sterically less** hindered  $\alpha$ -position is oxidized faster, therefore the methyl group of methyl ketones ( $R_1=H$ ) is preferentially oxidized over the other available  $\alpha$ -position;
- 3) The allylic positions in acyclic olefins are oxidized at very different rates and the reactivity depends on the substitution pattern of the substrate
- 4) For bicyclic olefins in which none of the rings contain more than 7 carbon atoms, the oxidation will not take place at the bridgehead position (Bredt's rule);
- 5) Rearrangement may occur if the preferred allylic position is adjacent to a quaternary carbon or a cyclopropyl ring.



# Riley oxidation



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