

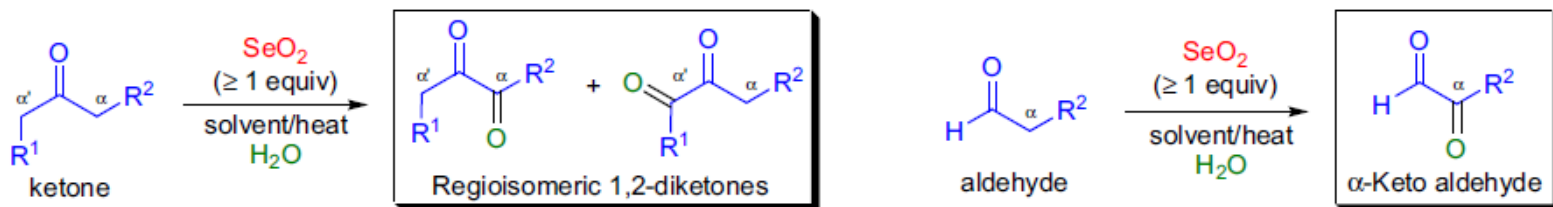
RILEY SELENIUM DIOXIDE OXIDATION

Zhou Guanshen

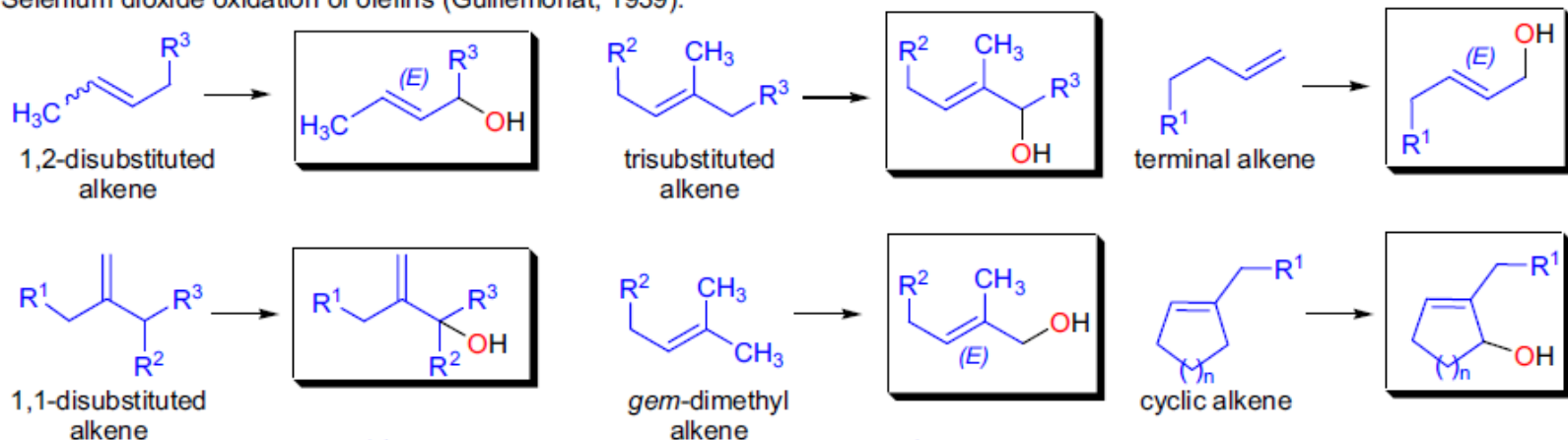
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Discovery

Selenium dioxide oxidation of ketones and aldehydes (Riley, 1932):



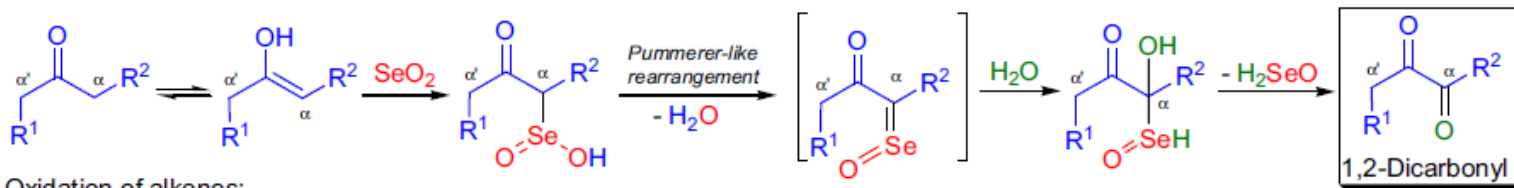
Selenium dioxide oxidation of olefins (Guillemonat, 1939):



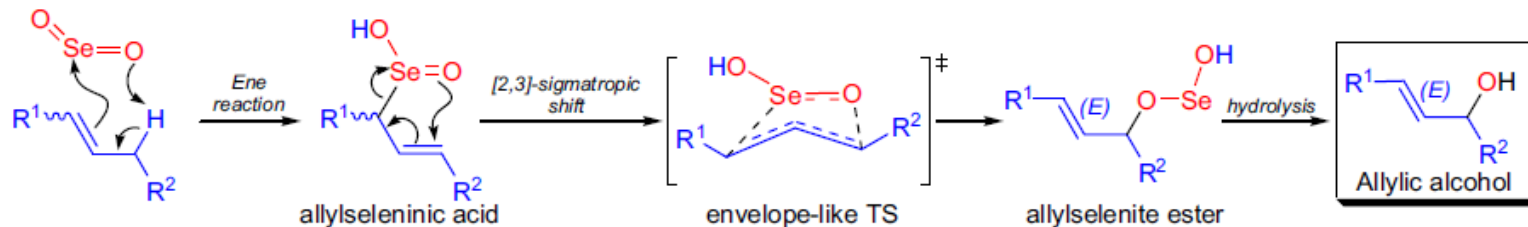
R^{1-2} = H, aryl, alkyl, substituted alkyl and aryl; R^3 = alkyl, aryl; n = 1-3

Mechanism

Oxidation of carbonyl compounds:



Oxidation of alkenes:



General features

- Low molecular weights are more reactive;
- Sterically less hindered α -position is oxidized faster;
- Rates of allylic positions in acyclic olefins:
 - 1,2-disubstituted alkenes: $\text{CH} > \text{CH}_2 > \text{CH}_3$;
 - Geminally disubstituted alkenes: $\text{CH} > \text{CH}_2 > \text{CH}_3$;
 - Trisubstituted alkenes: At the more substituted, $\text{CH}_2 > \text{CH}_3 > \text{CH}$;
 - Terminal olefins yield primary allylic alcohols;
 - Cyclic olefins occur in the ring and α to the more substituted carbon rather in side chain;
 - Unsubstituted double bond in cyclic olefins: $\text{CH}_2 > \text{CH}$.
- Bredt's rule: bridgehead position will not be oxidized in bicyclic olefins with both rings less than 7 carbons.

Synthetic applications

