Taming Oxygen-Rich Systems with Stereoelectronic Effects

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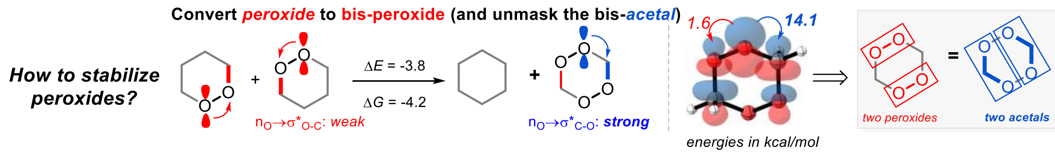
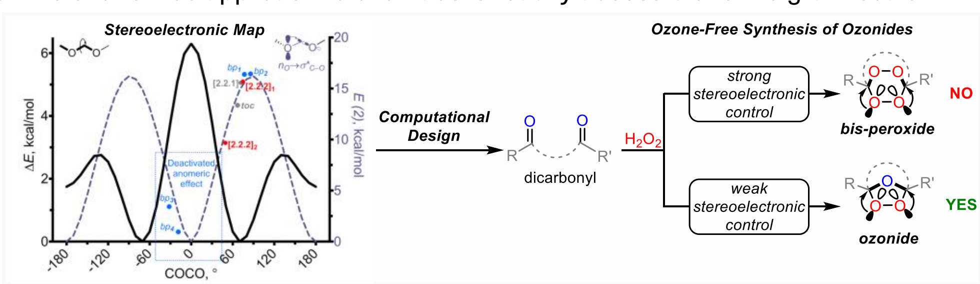
The unusual stability of bis-peroxides contradicts the conventional wisdom – some of them can melt without decomposition at temperatures exceeding 100 ºC. In this work, we disclose a stabilizing stereoelectronic effect that two peroxide groups can exert on each other. This stabilization originates from strong anomeric $n_O \rightarrow \sigma^*_{C-O}$ interactions that are absent in mono-peroxides, but reintroduced in molecules where two peroxide moieties are separated by a CH_2 group. The two unstable peroxides are transformed into two acetals.[1]



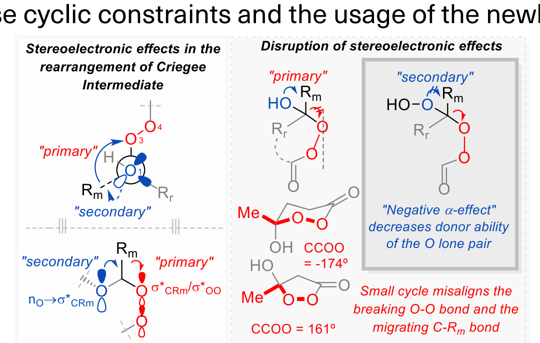
Scheme 1: Stabilizing peroxides with peroxides through anomeric interactions.

The value of stereoelectronic guidelines is illustrated by the discovery of a convenient, ozone-free synthesis of bridged secondary ozonides from 1,5-dicarbonyl compounds and H_2O_2. The expected tetraoxanes are not formed when the structural distortions imposed on the tetraoxacyclohexane subunit by a three-carbon bridge partially deactivate the anomeric effects. The ozone-free approach to ozonides is readily accessible to the gram-scale.[2]



Scheme 2: Ozone-free synthesis of ozone. Tuning ring sizes weakens stereoelectronic control that stabilizes bis-peroxides.

Finally, we have employed stereoelectronic effects to design a trap for the Criegee Intermediate (CI), the elusive intermediary for the Baeyer-Villiger reaction.[3] Our strategy involved the deactivation of transition-state stabilizing effects for the migratory step via precise cyclic constraints and the usage of the newly-found reverse α-effect.[4]



Scheme 3: Stereoelectronic control strategy for trapping the Criegee Intermediate.

References

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