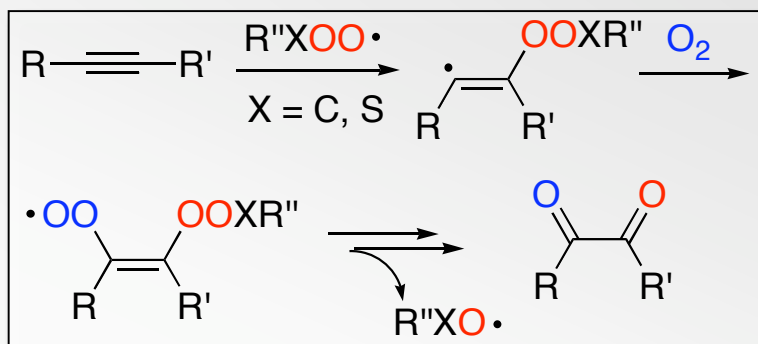


# Development of new pathways for the oxidative transformation of alkynes into highly reactive carbonyl compounds.

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- ❖ A major goal in synthetic chemistry is the development of oxidation procedures that use the most abundant (and cheapest) oxidant, molecular oxygen, under non-toxic conditions.
- ❖ We have discovered a *novel mild and metal-free activation of molecular oxygen* that enables transformation of alkynes into 1,2-diketones mediated by peroxy radicals.



Experimental and computational studies revealed insight into the mechanism

- ❖ addition of a peroxy radical  $R''XOO\cdot$  (where  $X = C$  or  $S$ ) to the alkyne gives a vinyl radical, which is trapped by oxygen
- ❖ subsequent fragmentation of the peroxy O-O bond with release of an alkoyl radical  $R''XO\cdot$  gives a Crigee-type intermediate, which decomposes to the 1,2-diketone
- ❖ this oxidation is the first example for the synthetic application of thiylperoxy radicals  $R''SOO\cdot$  reported in literature.

