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 peroxyl radicals.

❖ Solution and in the gas phase experiments, in combination with computational studies revealed insight into the mechanism of these transformations.

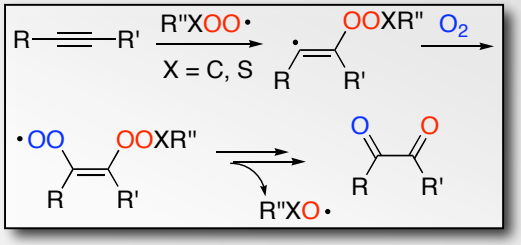
❖ **Solution phase experiments:** Addition of peroxyl radicals R''XOO• (X = C or S) to alkynes gives vinyl radicals, which are trapped by oxygen

❖ Subsequent fragmentation of O-O bond with release of an alkoyl radical R''XO• gives a Crigee-type intermediate, which decomposes to the 1,2-diketone

❖ With X = S: This oxidation is the first example for the synthetic application of thiylperoxyl radicals R''SOO• reported in literature.

❖ **Gas phase experiments:** Identification of intermediates and products and kinetic data (for the first time).

a) In solution (presence of O_2)



b) In gas phase (absence of O_2)