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Oxo-functionalization of unsaturated lipids by a photooxidation / molybdate catalysis sequence

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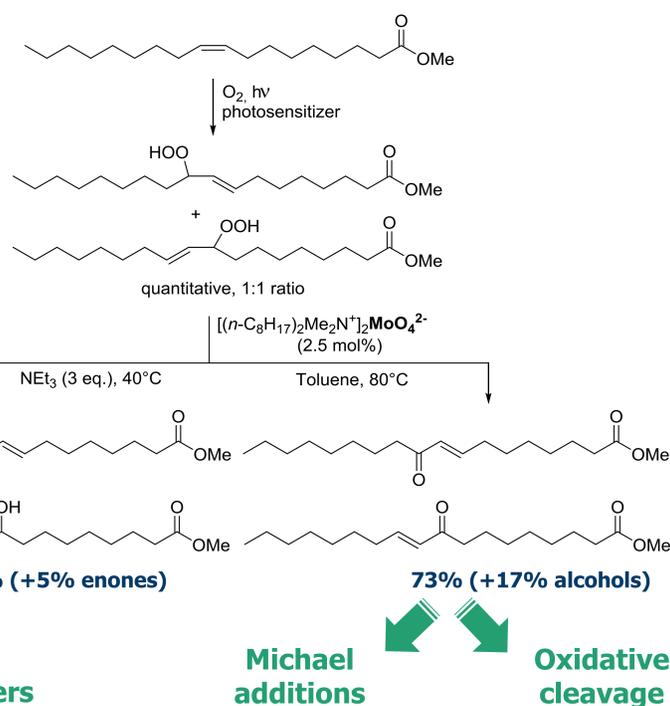
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Objective : green access to keto- or hydroxy derivatives of unsaturated fatty Acids

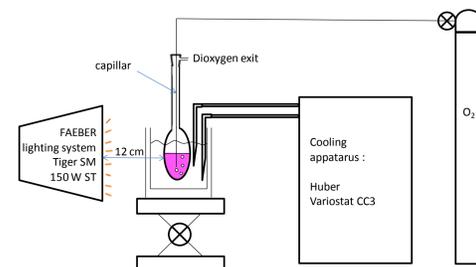
Overall sequence :

Depending of the reaction conditions, either the enones or the allylic alcohols are obtained in good selectivity with the same catalyst, an organosoluble ammonium salt of molybdate anion without any additional ligand. The catalyst can be easily separated after the reaction by aqueous washes.



Photooxidation step :

Performed in dichloromethane (1.5 g of methyl oleate / 10 mL) using *meso-tetra*-phenylporphyrine (TPP, 2 mg) as photosensitizer under irradiation of high pressure sodium lamp and dioxygen bubbling.



Full conversion in 8 hours.

Choice of DCM as solvent because :

- non flammable
- good solubility of the FAMES
- easily removable due to its low boiling point, avoid to heat the peroxides
- rather long lifetime of ¹O₂ in this solvent ($t_{1/2} = 99 \mu\text{s}$).

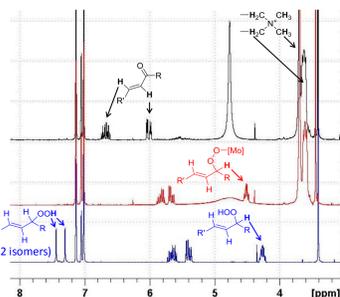
Note: the reactivity rate constant of methyl oleate is twice higher than its quenching rate constant with singlet dioxygen. ($k_r = 2.4 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ vs $k_q = 1.2 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ in CHCl₃ at 20 °C)

Tanielian, C.; Mechin, R. Reaction and quenching of singlet molecular oxygen with esters of polyunsaturated fatty acids. *Photochem. Photobiol.* **1994**, *59*, 263-268.

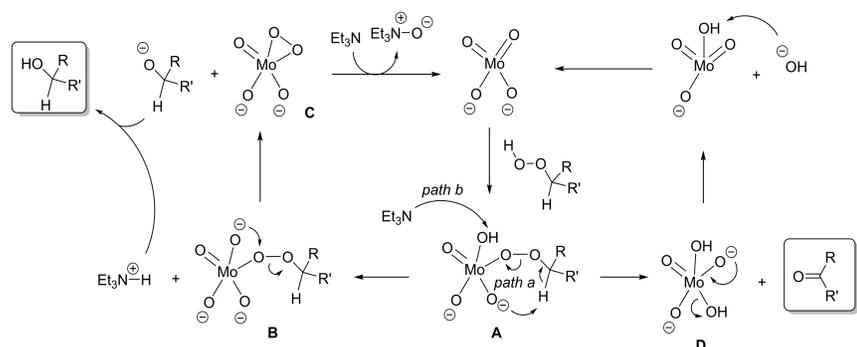
Proposed mechanism of the molybdate catalyzed reactions:

¹H NMR proof of an adduct between the hydroperoxide and the molybdate anion :

¹H NMR in Toluene-d₆ of methyl oleate hydroperoxides alone (blue) and in presence of stoichiometric amount of [C₈H₁₇Me₂N]₂MoO₄²⁻, first after 15 minutes at room temperature (red), then after 1 hour at 80 °C (black) :



Dual behavior of the catalyst depending of the conditions :



Notes:

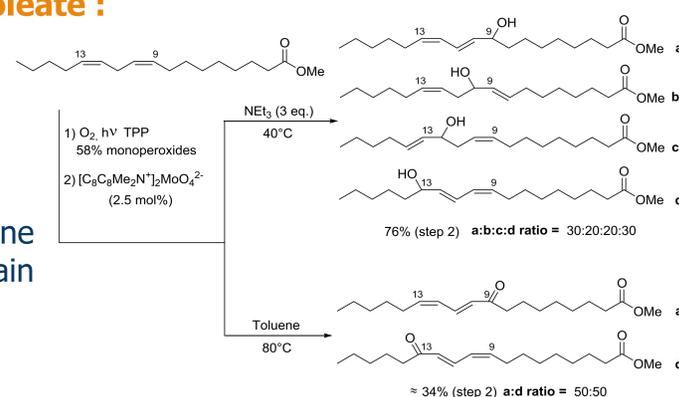
- triethylamine-*N*-oxide quantitatively observed in ¹H NMR
- "reduction" much slower with the more nucleophilic but less basic pyridine instead of triethylamine
- "reduction" much faster and more selective with dodecanthiol, but more expensive material and more difficult to separate than the volatile triethylamine

Substrates scope :

Case of methyl linoleate :

4 hydroperoxides isomers are formed during the photo-oxidation.

The (α,β)-(γ,δ)-dienone isomers are the main isolated ones



Other olefins :

NMR yields of dehydration into enone or reduction into allylic alcohol of allylic hydroperoxides (0.25 mmol) from several alkenes using [C₈H₁₇Me₂N]₂MoO₄ (5 mol%) catalyst. Conditions A = toluene (V_T = 0.5 mL), 80 °C, 4h. Conditions B = triethylamine (0.75 mmol), 40 °C, 4h. Conversions = 100%.

substrates	Keto/hydroxy derivatives	¹ H NMR yield
		A : 55/26 B : 22/66
		A : 37/19 B : 9/86
		A : 51 ^b /12 B : 33 ^b /42 ^a : (hydroperoxide already contains 11% aldehyde after photooxidation)
		A : 78 ^b /9 B : 27/67 ^b : mixture 60:12 ketone:aldehyde coming from Schenck rearrangement
		A : 31/(0+7) ^c B : 0/(48 + 48) ^c : + other byproducts
		A : (20+12)/(11+15) B : (2+0)/(37+40)