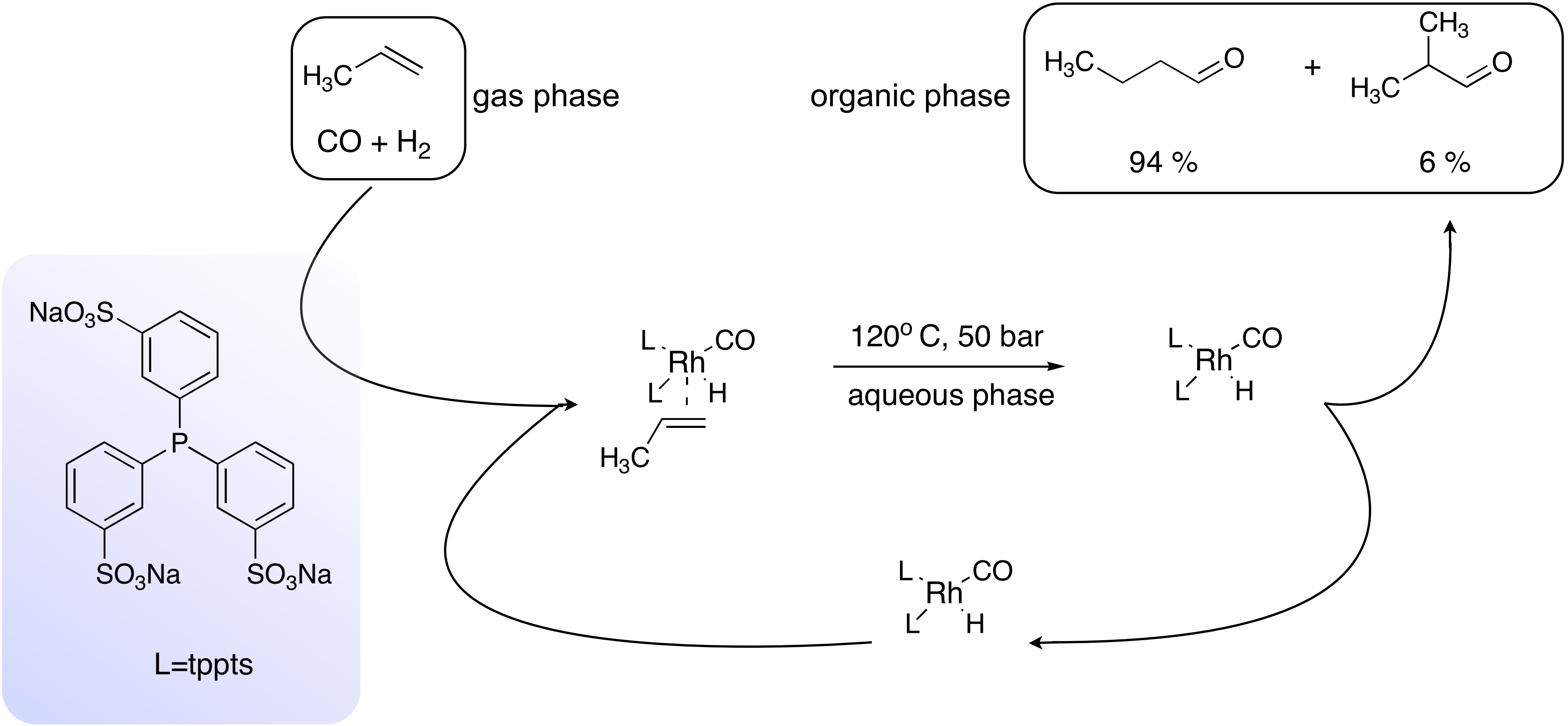
Milieux aqueux

- Upside
  - Non toxic (liquid + vapor)
  - Non flammable
  - Abundantly available (better availability than organic solvent in less developed countries)
  - Inexpensive

- Downside
  - Corrosion
  - Heat sink
  - High boiling point
    - Water-based processes are energy intensive
    - Large amount of energy to dry dyed fibers
  - Solubility of organic matter is generally poor
  - Reaction range narrower than organic solvents
  - A vital resource to be conserved and protected
    - 100 liters of water needed to dye 1 kg of fiber
  - Expands when freezes

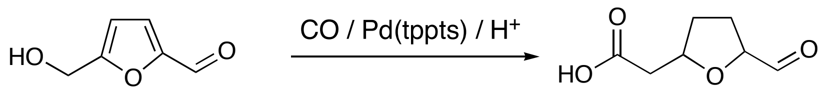
Milieux aqueux



Rhône-Poulenc/Ruhrchemie process for aqeous biphasic hydroformylation

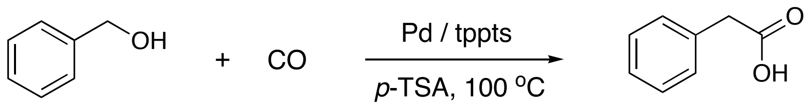
Milieux aqueux

Alcohol carbonylation in an aqueous biphasic system

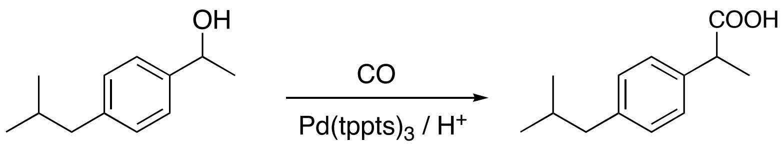


HMF

FFA



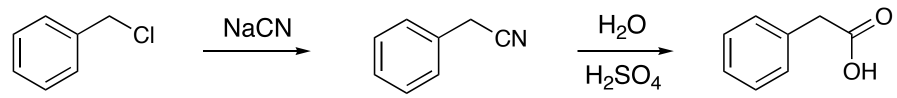
77 % yield
100 % sel.



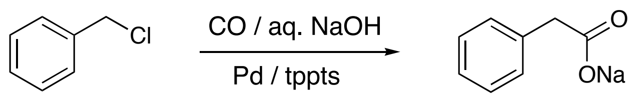
Ibuprofen

Aqueous biphasic carbonylation

Existing process



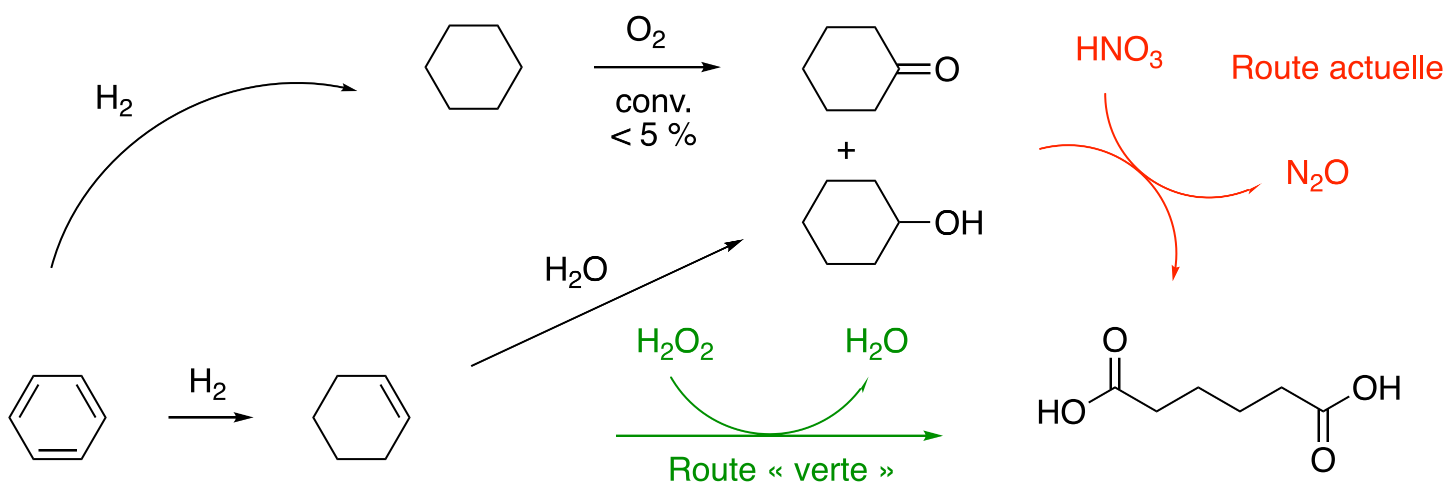
New process



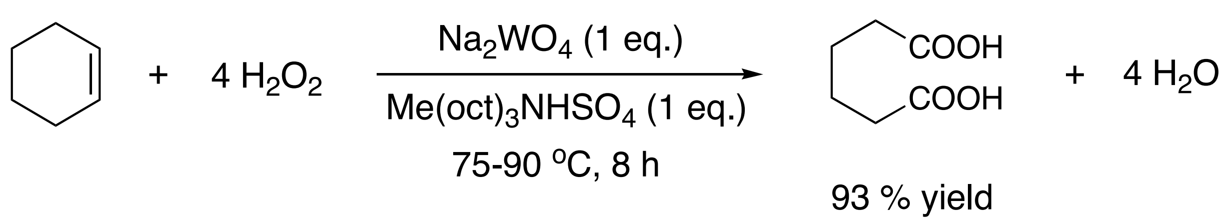
Papadogianakis, G.; Maat, L.; Sheldon, R. A., *J. Mol. Catal, A: Chem.*, **1997**, *116*, 176–190
Papadogianakis, G.; Maat, L.; Sheldon, R. A., *J. Chem. Technol. Biotechnol.* **1997**, *70*, 83–91
Kohlpainter, W.; Beller, M., *J. Mol. Catal. A: Chem*, **1997**, *116*, 259–267
Green Solvents for Sustainable Organic Synthesis: State of Art", Sheldon, R. A., *Green Chem.*, **2004**, *7*, 267–278

Milieux aqueux

- *Synthèses de l'acide adipique*



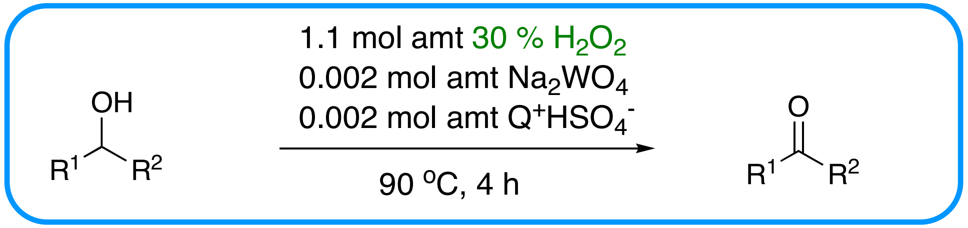
- *Synthèse verte de l'acide adipique*

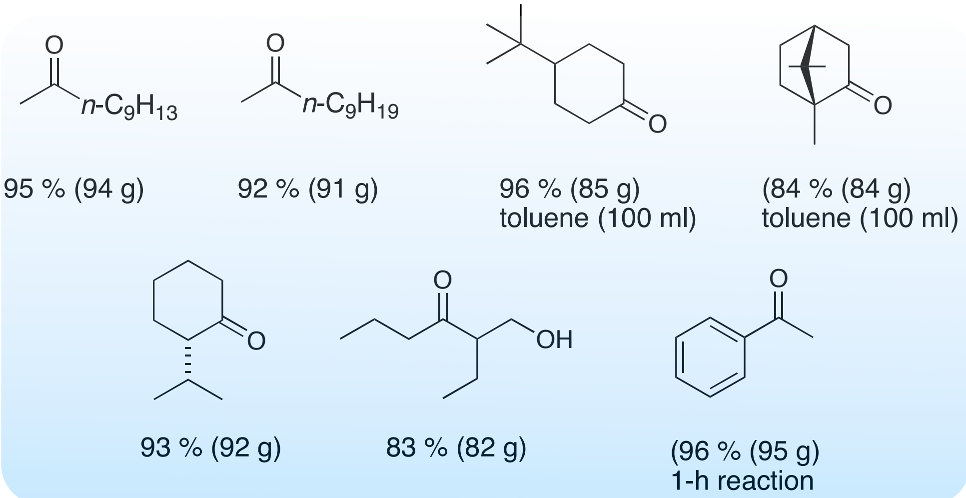


"Green Oxidation with Aqueous Hydrogen Peroxide", Noyori, R.; Aoki, M.; Sato, K., *Chem. Commun.* **2003**, 1977–1986

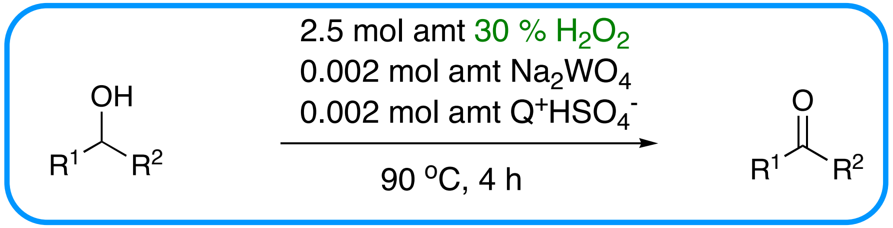
Milieux aqueux

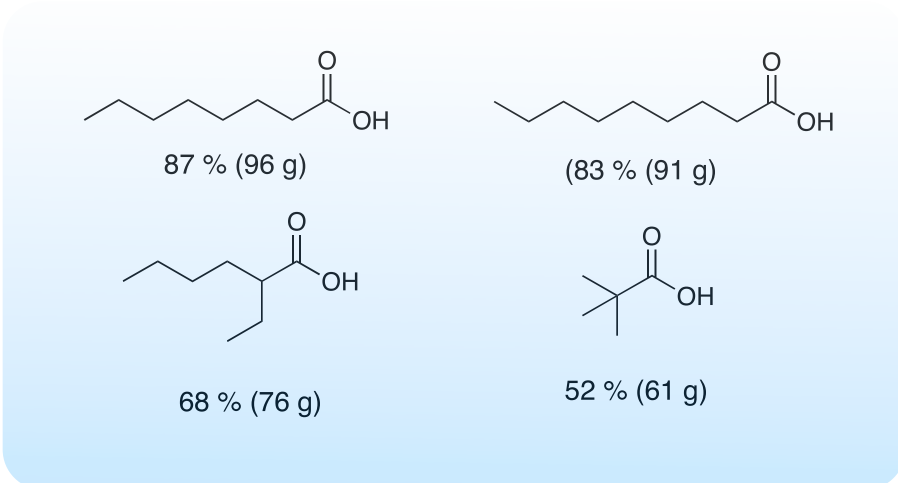
Oxidation of secondary alcohols to ketones





Oxidation of primary alcohols to carboxylic acids



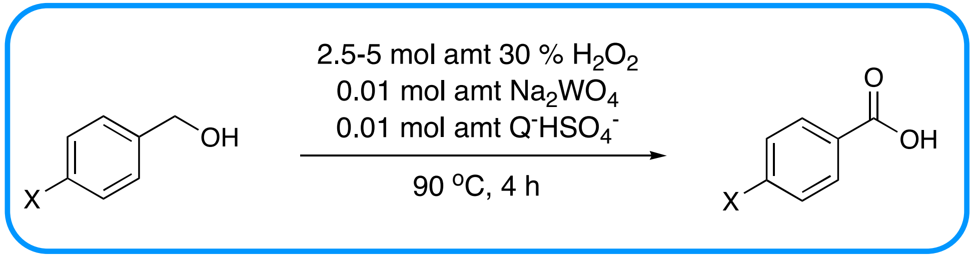


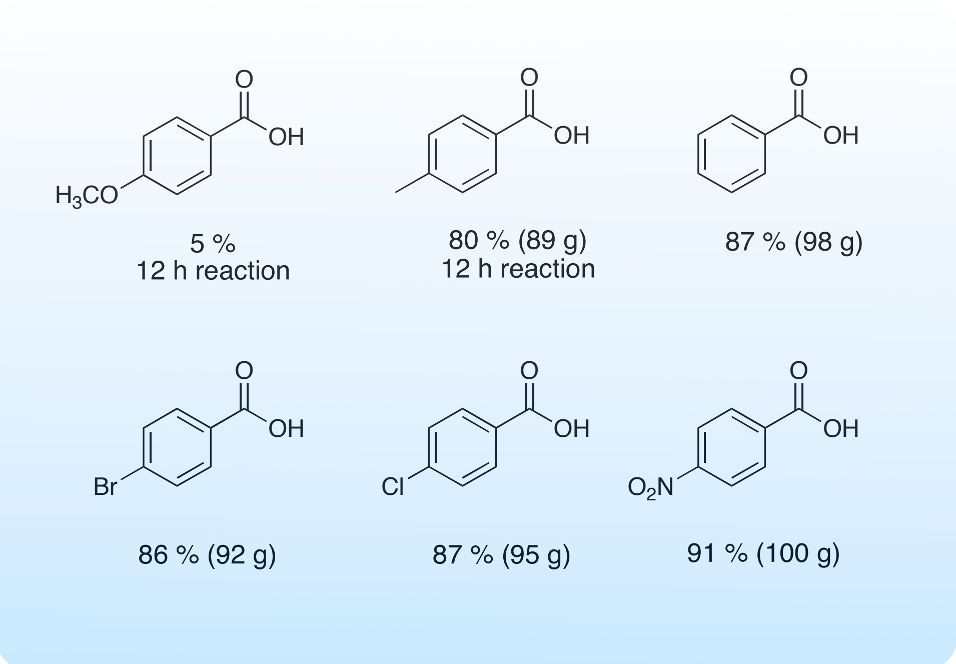
($Q^+HSO_4^-$) = methyltrioctylammonium hydrogensulfate [$CH_3(n\text{-}C_8H_{17})_3N^+HSO_4^-$]

"Green Oxidation with Aqueous Hydrogen Peroxide", Noyori, R.; Aoki, M.; Sato, K., *Chem Commun.* **2003**, 1977–1986

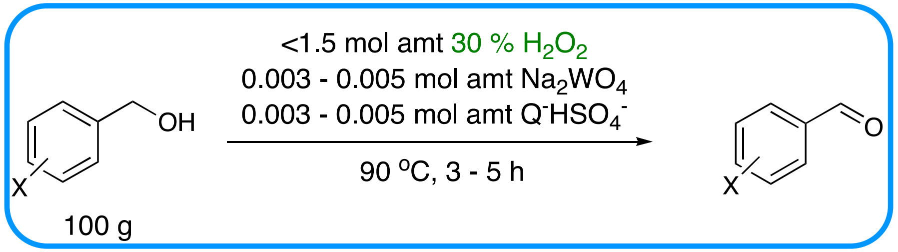
Milieux aqueux

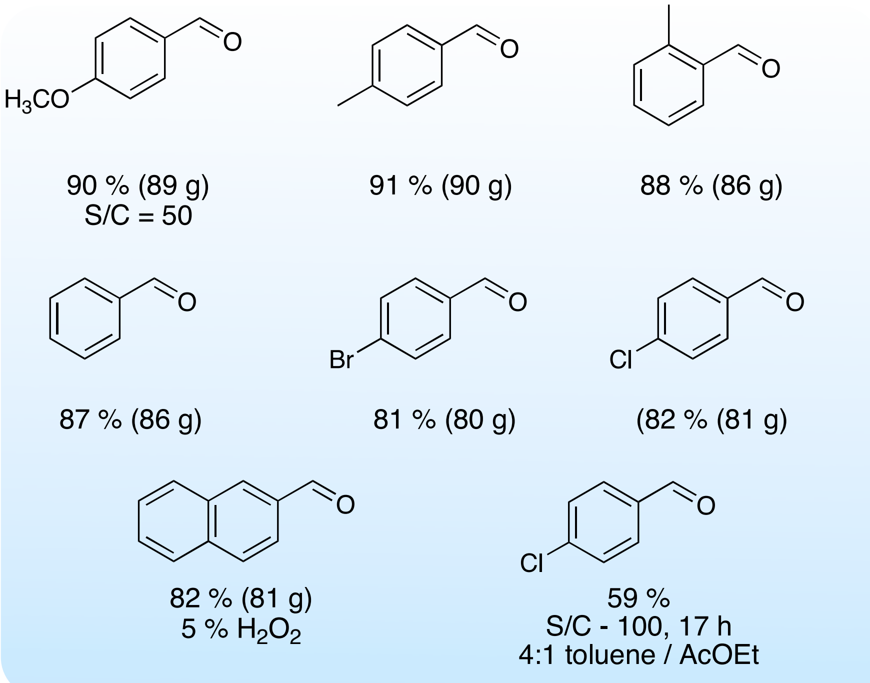
Oxidation of secondary alcohols to ketones





Oxidation of primary alcohols to carboxylic acids





"Green Oxidation with Aqueous Hydrogen Peroxide", Noyori, R.; Aoki, M.; Sato, K., *Chem Commun.* **2003**, 1977–1986

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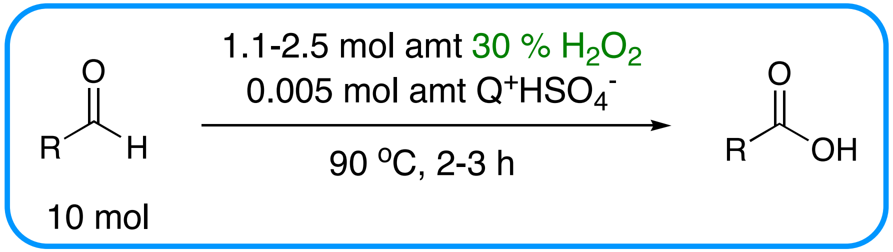
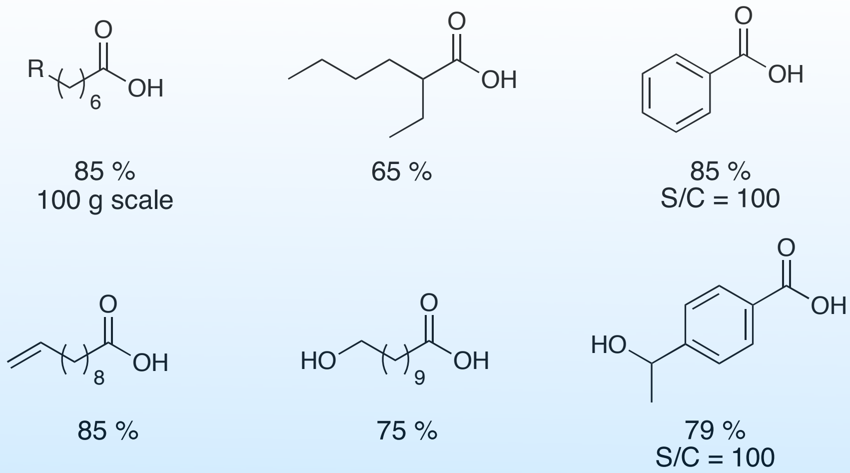
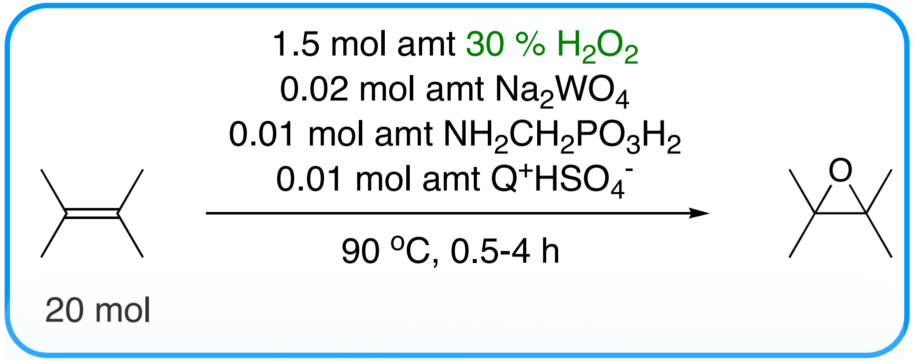
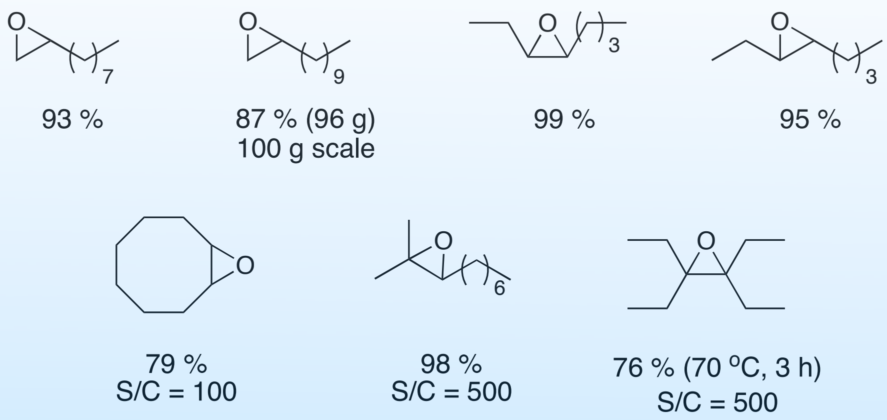
Solvent- and metal-free oxidation of aldehydes





Epoxidation of simple olefins





"Green Oxidation with Aqueous Hydrogen Peroxide", Noyori, R.; Aoki, M.; Sato, K., *Chem Commun.* **2003**, 1977–1986

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- Diels Alder reaction
  - Marked rate acceleration in aqueous media
- Metathesis - from the Nobel Committee:
  - “Metathesis is used daily in the chemical industry, mainly in the development of pharmaceuticals and of advanced plastic materials. Thanks to the Laureates' contributions, synthesis methods have been developed that are
    - more efficient (fewer reaction steps, fewer resources required, less wastage),
    - simpler to use (stable in air, at normal temperatures and pressures) and
    - environmentally friendlier (non-injurious solvents, less hazardous waste products).
  - This represents a great step forward for "*green chemistry*", reducing potentially hazardous waste through smarter production. Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment.”

“Reaction of C-H bonds in Water”, Herrerias, C. I; Yao, X.; Li, Z.; Li, C.-J., *Chem. Rev.* **2007**, *107*, 2546–2563

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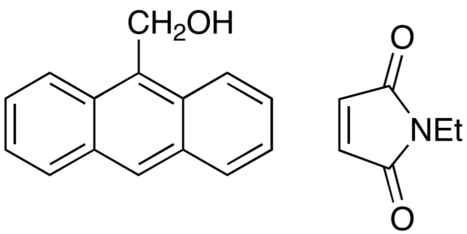
Relative rates of Diels-Alder reactions performed in water and in organic solvents

Reactants	T (°C)	Isooctane	Methanol	Water
	20	1	13	740
	30	1	2	31
	45	1	0.43	28

"Salt Effects on Diels-Alder Reaction Kinetics", Kumar, A., *Chem. Rev*. **2001**, 101, 1–19
"Recent Advances in Lewis Acid Catalyzed Diels-Alder Reactions in Aqueous Media"
Fringuelli, F.; Piermatti, O.; Pizzo, F.; Vaccaro, L., *Eur. J. Org. Chem.* **2001***, 3,* 439–455

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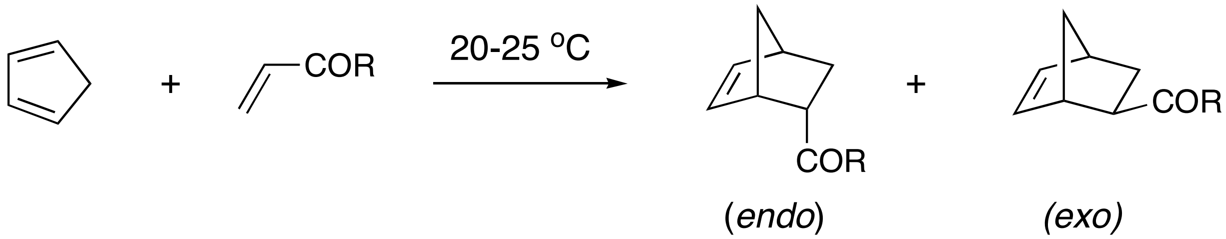
endo/exo Diastereoselectivities of Diels-Alder reactions performed in water and in organic solvents



Medium	*endo / exo* R = Me	*endo / exo* R = OMe
None	3.85	2.9
Isooctane		2.3
Ethanol	8.5	5.2
1-Butanol		5.0
Formamide		6.7
N-Methylformamide		4.7
Water	21.4	9.3

"Salt Effects on Diels-Alder Reaction Kinetics", Kumar, A.; *Chem. Rev*. **2001**, 101, 1–19
"Recent Advances in Lewis Acid Catalyzed Diels-Alder Reactions in Aqueous Media"
Fringuelli, F.; Piermatti, O.; Pizzo, F.; Vaccaro, L.; *Eur. J. Org. Chem.* **2001**, *3,* 439–455

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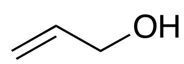
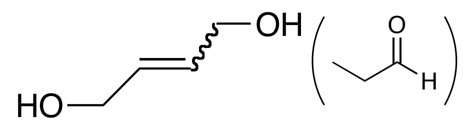
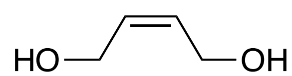
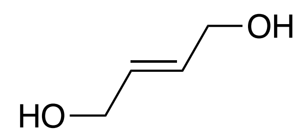
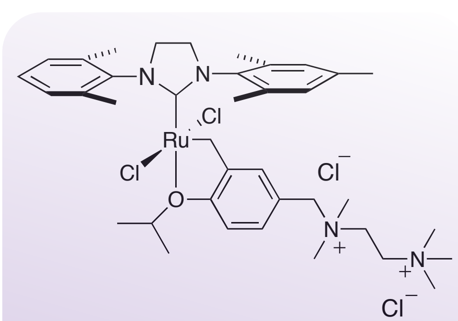
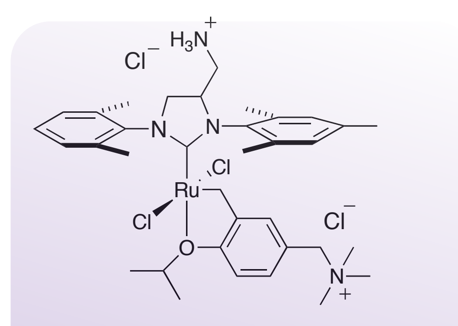
- *Métathèse croisée dans l'eau*

Catalyst	Substrate	*t* (h)	Product	Conversion (%)	*E/Z*
4 (b)		12		> 95	15:1
5		24		82 (+4)	13:1
6		6		69 (+12)	19:1
4 (b)		12		94	-
5 (c)		24		92	-
6 (c)		2		94	-

(a) Reactions were performed at 45 °C with 5 mol % catalyst and an initial substrate concentration of 0.2 M in D_2O.
(b) Reactions were performed at 45 °C with 5 mol % catalyst and an initial substrate concentration of 0.2 M in D_2O or H_2O.
(c) Reactions were performed at 30 °C.



5



6

"Small-Molecule N-heterocyclic-Carbene-Containing Olefin-Metathesis Catalysts for Use in Water", Jordan, J.-P.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 5152–5155