Epoxidation of Olefins Using Molecular Oxygen

Zhongxing Huang
Sep 16th, 2015

Ten challenges for catalysis

Many unsolved problems face the catalysis research community, says James F. Roth, retired corporate chief scientist at Air Products & Chemicals. He has selected 10 challenges that typify the present needs of industrial catalysis:

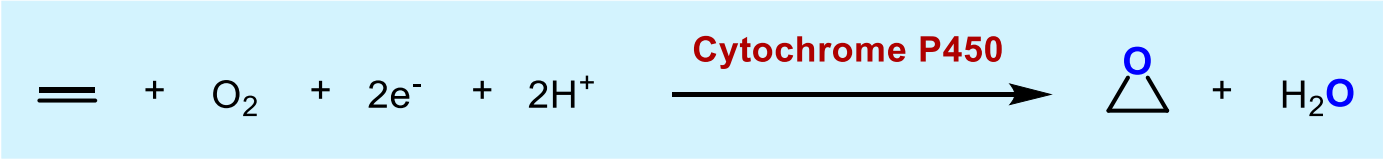
- A new catalyst for low-temperature oxidation of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid. Sulfuric acid is the largest volume chemical made in the U.S., and the production process has had only incremental improvements througout many years. What is needed is not another incremental improvement but a substantially different way of making the acid.
- An oxidation catalyst for selective oxidation of methane to methanol. There is no such catalyst at present. Most of the research in this area focuses on high-temperature oxidation catalysts. A low-temperature, liquid-phase catalyst would be very desirable.
- A new catalyst for the facile decomposition of nitrogen oxides to molecular nitrogen and oxygen in the presence of water and carbon dioxide. This would be a great advance in environmental protection.
- A high-conversion, high-selectivity catalyst for production of ethylene, propylene, and styrene from their respective alkanes. Ethylene is the industry's most important feedstock, with about 40% of all organic chemicals production based on it. The usual method is isothermal cracking, which generates many by-products and is both capital- and energy-intensive.
- A selective catalyst for oxidative coupling of methanol to ethylene. This would shift the feedstock base from ethylene to methanol.
- A selective catalyst for producing phenol by direct oxidation of benzene using molecular oxygen rather than the present cumene-based process.
- Catalysts for the selective, direct synthesis of hydrogen peroxide from hydrogen and oxygen under mild conditions.
- Low-temperature selective oxidation catalysts for the epoxidation of ethylene by molecular oxygen.
- Synthesis of aromatic amines via the direct interaction of aromatics with ammonia.
- Anti-Markovnikov addition of water or ammonia to olefins to directly synthesize primary alcohols or amines.

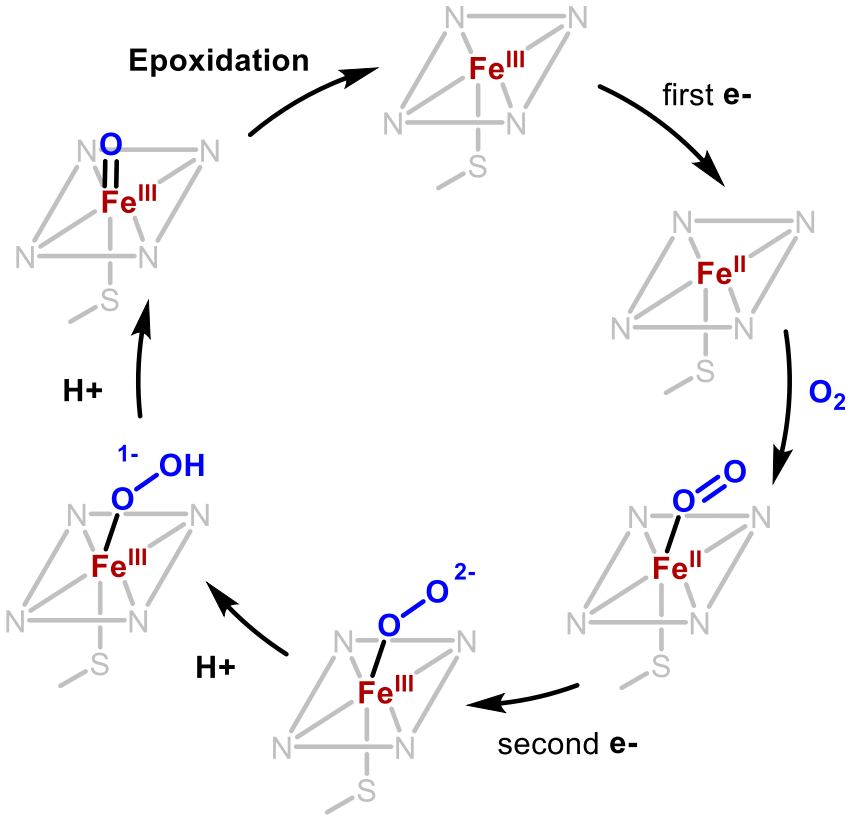
Key points

- Low temperature
- Selective

May 31st, 1993, C&EN News.

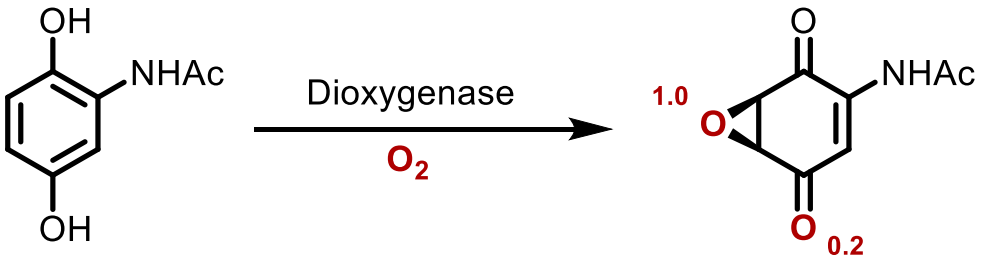
Monooxygenase catalyzes the incorporation of **one atom** of oxygen into the product





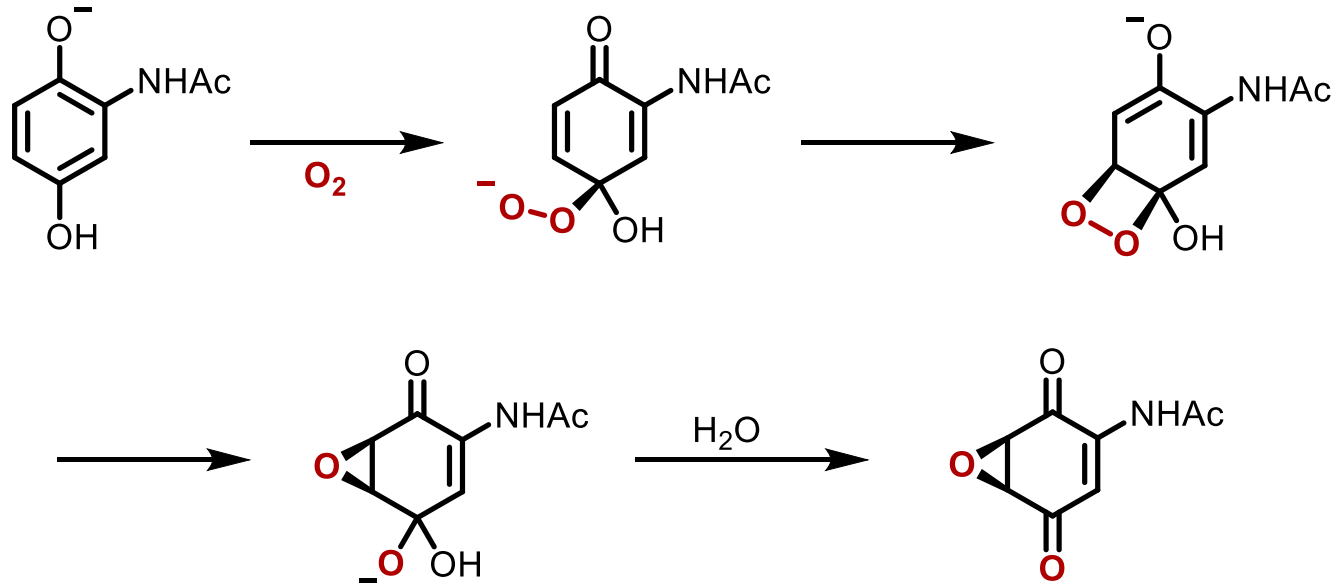
Iron-Containing Enzymes, RSC Publishing, 2011.

Dioxygenase incorporates **both oxygen atoms** into the product



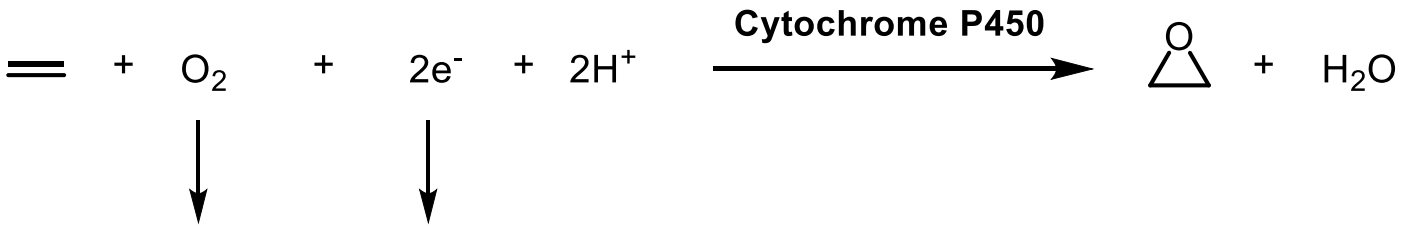
antibiotic LL-C10037α

Proposed pathway:



Shen, B.; Gould, S. J. *Biochemistry* **1991**, *30*, 8936.
Gould, S. J.; Kirchmeier, M. J.; LaFever, R. E. *J. Am. Chem. Soc.* **1996**, *118*, 7663.

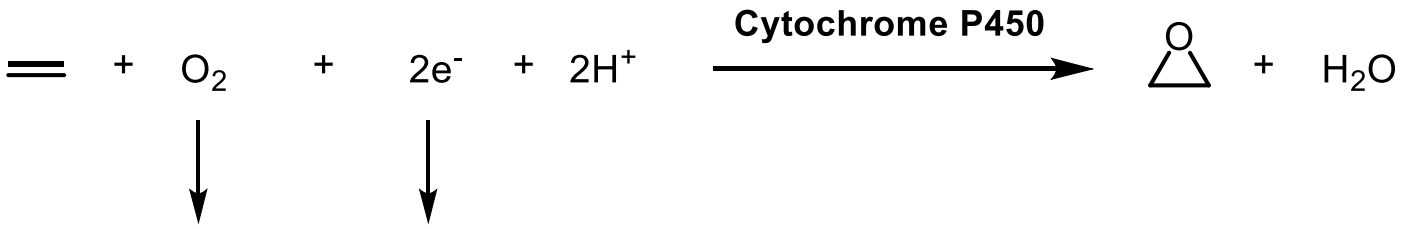
Monooxygenase catalyzes the incorporation of **one atom** of oxygen into the product



- **Ideal system should avoid use of reductants**

Dioxygenase incorporates **both oxygen atoms** into the product

Monooxygenase catalyzes the incorporation of **one atom** of oxygen into the product

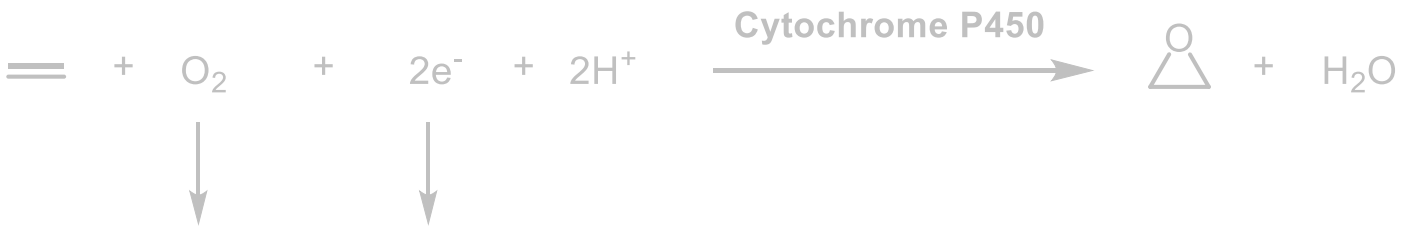


- **Ideal system should avoid use of reductants**

~~**Dioxygenase** incorporates **both oxygen atoms** into the product~~

Ideal Dioxygenase incorporates **both oxygen atoms** into the **epoxide**

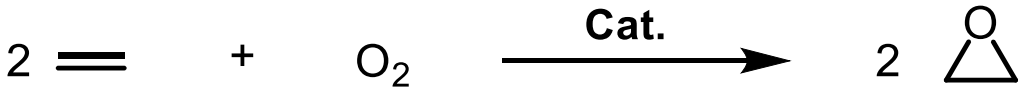
Monooxygenase catalyzes the incorporation of **one atom** of oxygen into the product



- **Ideal system should avoid use of reductants**

~~**Dioxygenase** incorporates **both oxygen atoms** into the product~~
Ideal Dioxygenase incorporates **both oxygen atoms** into the **epoxide**

Ultimate Goal



- Top chemicals produced in US (2004,10^3 ton)

1	sulfuric acid	35954
2	nitrogen	30543
3	ethylene	25682
4	oxygen	25568
5	propylene	15345
6	chlorine	12166
7	ethylene dichloride	12163
8	phosphoric acid	11463
9	ammonia	10762
10	sodium hydroxide	9508
11	benzene	7675
12	nitric acid	6703
13	ammonium nitrate	6021
14	ethylbenzene	5779
15	urea	5755
16	styrene	5394
17	hydrochloric acid	5012
18	ethylene oxide	3772
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Ethylene Oxide (EO)

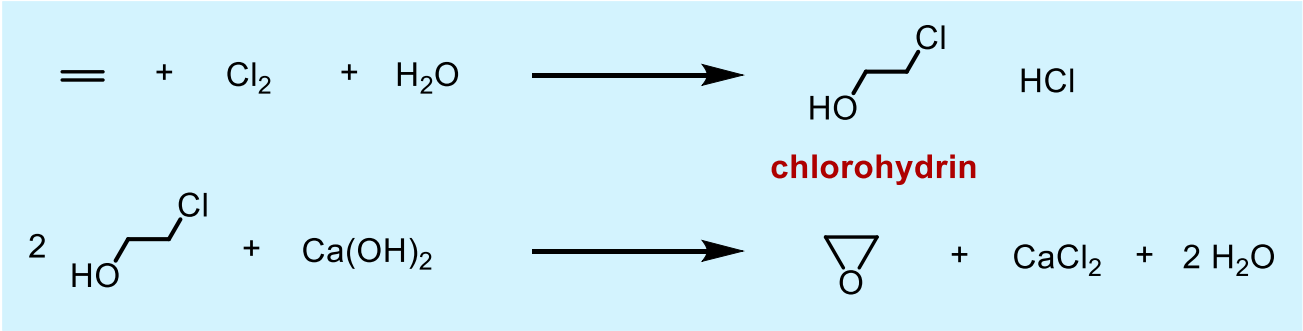
- Worldwide consumption 14.7 million tons (2002)
- Takes up >=10% ethylene production
- US$ 1.66-1.88/kg (2006)
- Washing/dyeing, electronics, pharmaceuticals, pesticides, textiles, papermaking, automobiles, oil recovery and oil refining.

Propylene Oxide (PO)

- Worldwide consumption 6.74 million tons (2003)
- Takes up >=10% propylene production
- US$ 1.88-2.03/kg (2006)
- Polyurethane polyols (60-65%), propylene glycols (20-25%), P-series glycol ethers (3-5%) and other

Kirk Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, 2001.

- **Chlorohydrin Process**
  - Discovered in 1859
  - Phased out in 1940s



- **Chlorohydrin Process**
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  - Phased out in 1940s
- **Direct Oxidation methods (Ag/O_2)**
  - Patented in 1931 by Lefort
  - Union Carbide (first to use)
  - Scientific Design Co. (25% world production)
  - Shell (40% world production)

Shell process (state of the art)

$Ag/\alpha\text{-}Al_2O_3$ + Re + Cs promoters/O_2;
230-280 °C, 10-35 atm;
conv. ~ 10%, **selectivity ~ 85%**, Yield 40-440g/kg(cat)/h

US Patent 6717001 B2, Apr. 2004

EO production

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230-280 °C, 10-35 atm;
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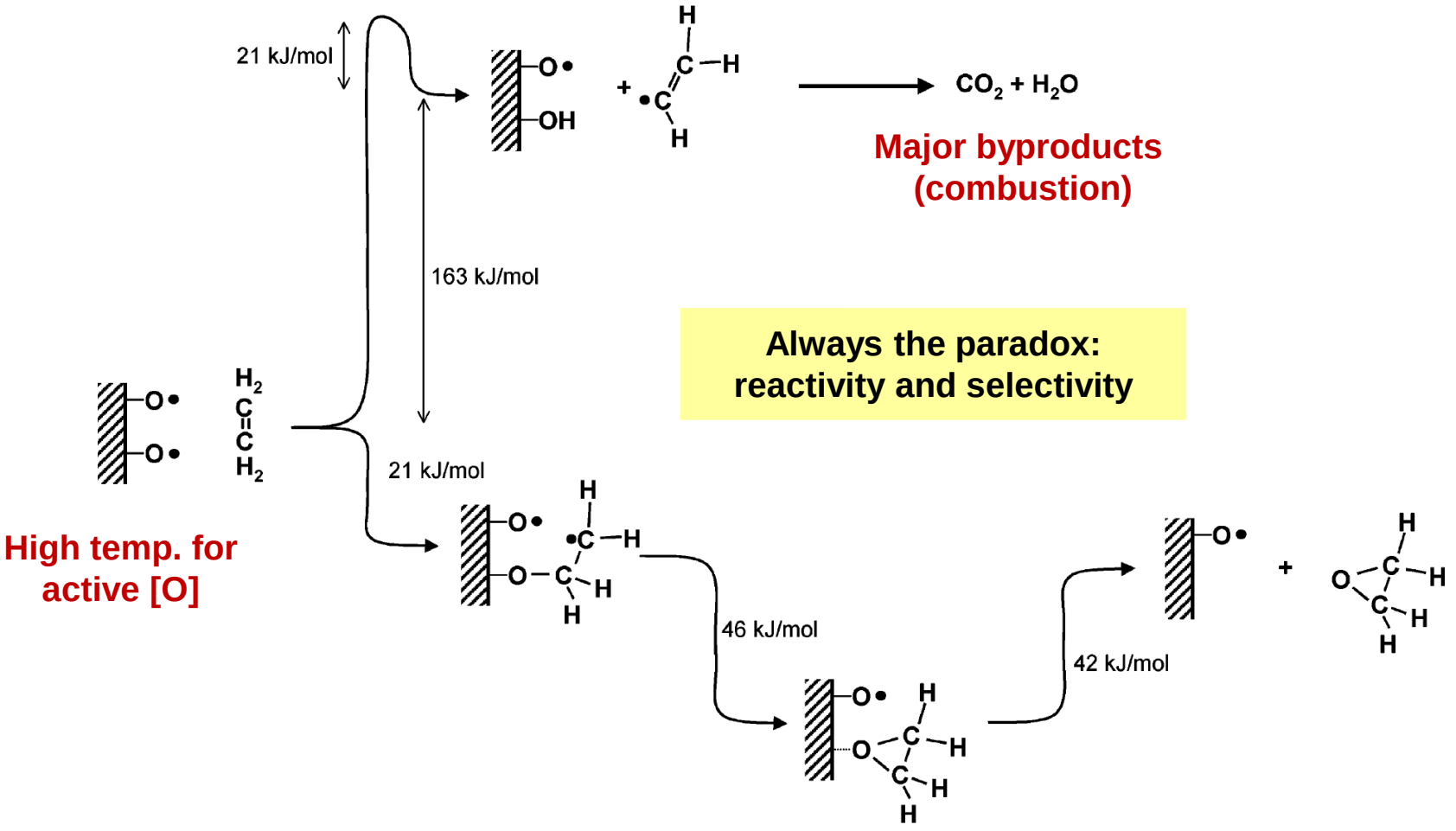
If you could increase the selectivity by **1%** for the Shell Process, considering EO world production as 14.7 million tons, Shell's share as 40% and EO price as 1.66 US$/kg, the extra earning each year would be **110 million US$**.

That's your salary working as a TA at UT for **4583 years**.

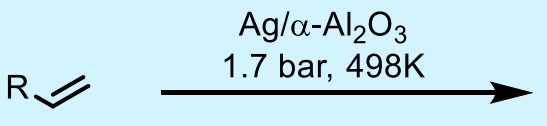
US Patent 6717001 B2, Apr. 2004

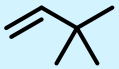
- **Origins of High temperature and selectivity**



Ind. Eng. Chem. Res, **2006**, *45*, 3447.

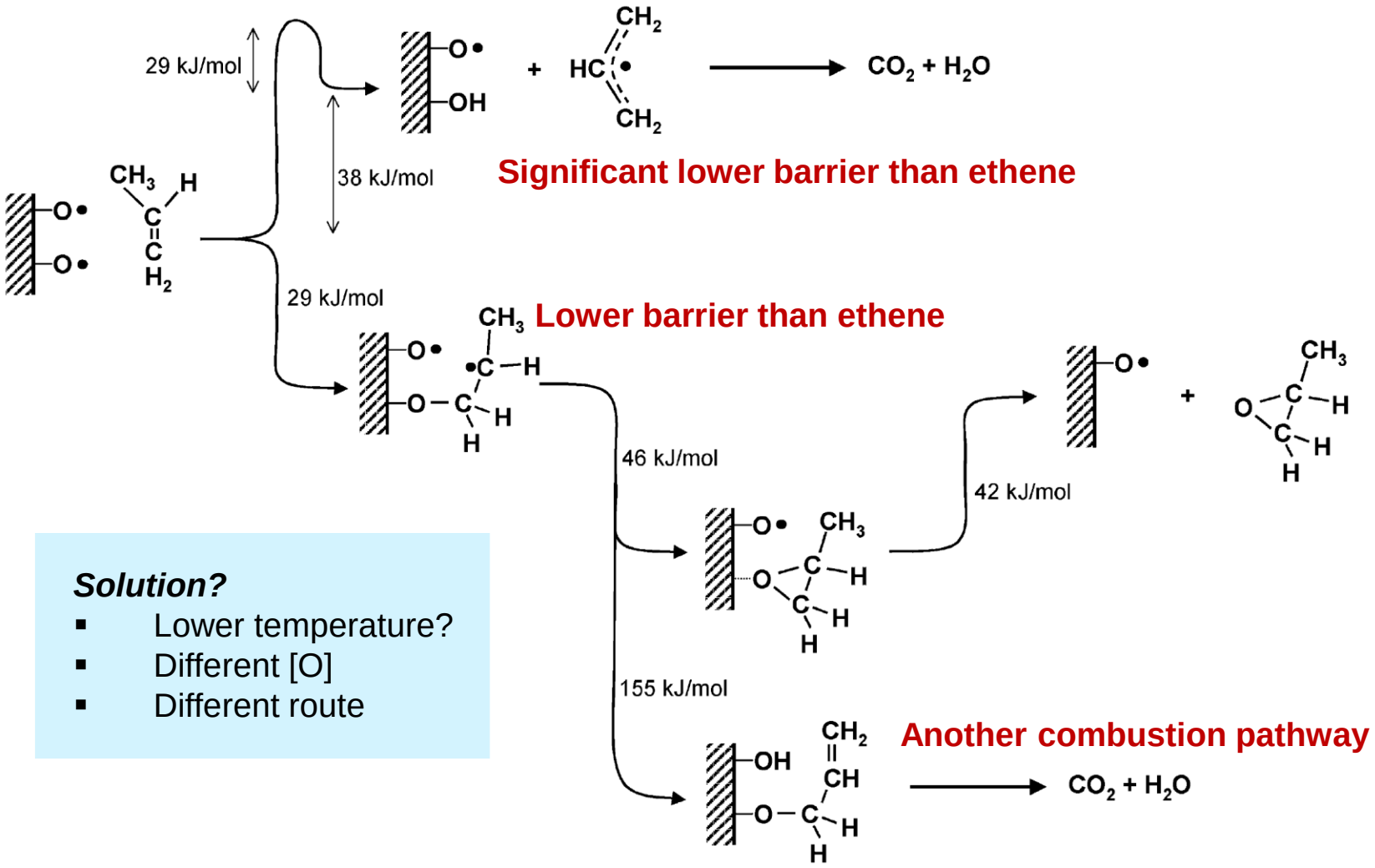
- **How about Ag/O2 system for PO production**



Gas	Conversion (%)	Selectivity (%)
	17.8	47.4
	7.5	**6.0**
	4.0	25.0

Ind. Eng. Chem. Res, **2006**, *45*, 3447.

- **Origins of low selectivity**

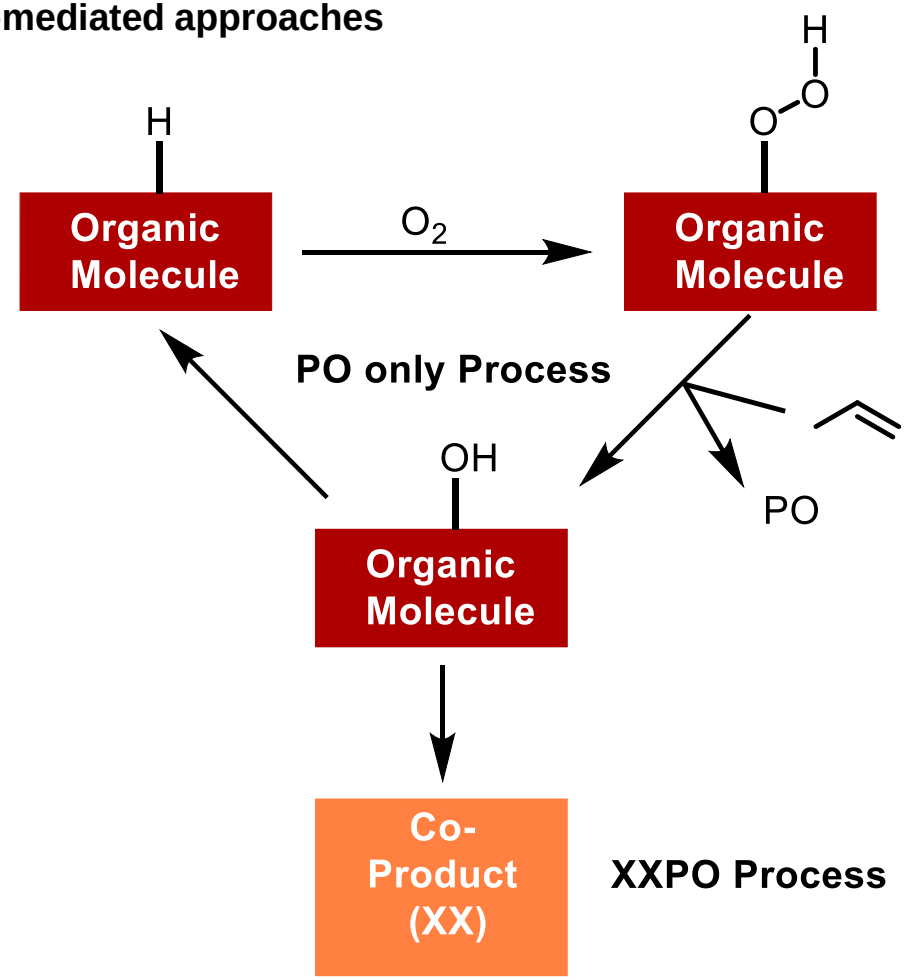


Solution?

- Lower temperature?
- Different [O]
- Different route

Ind. Eng. Chem. Res, **2006**, *45*, 3447.

- **Organic peroxide-mediated approaches**

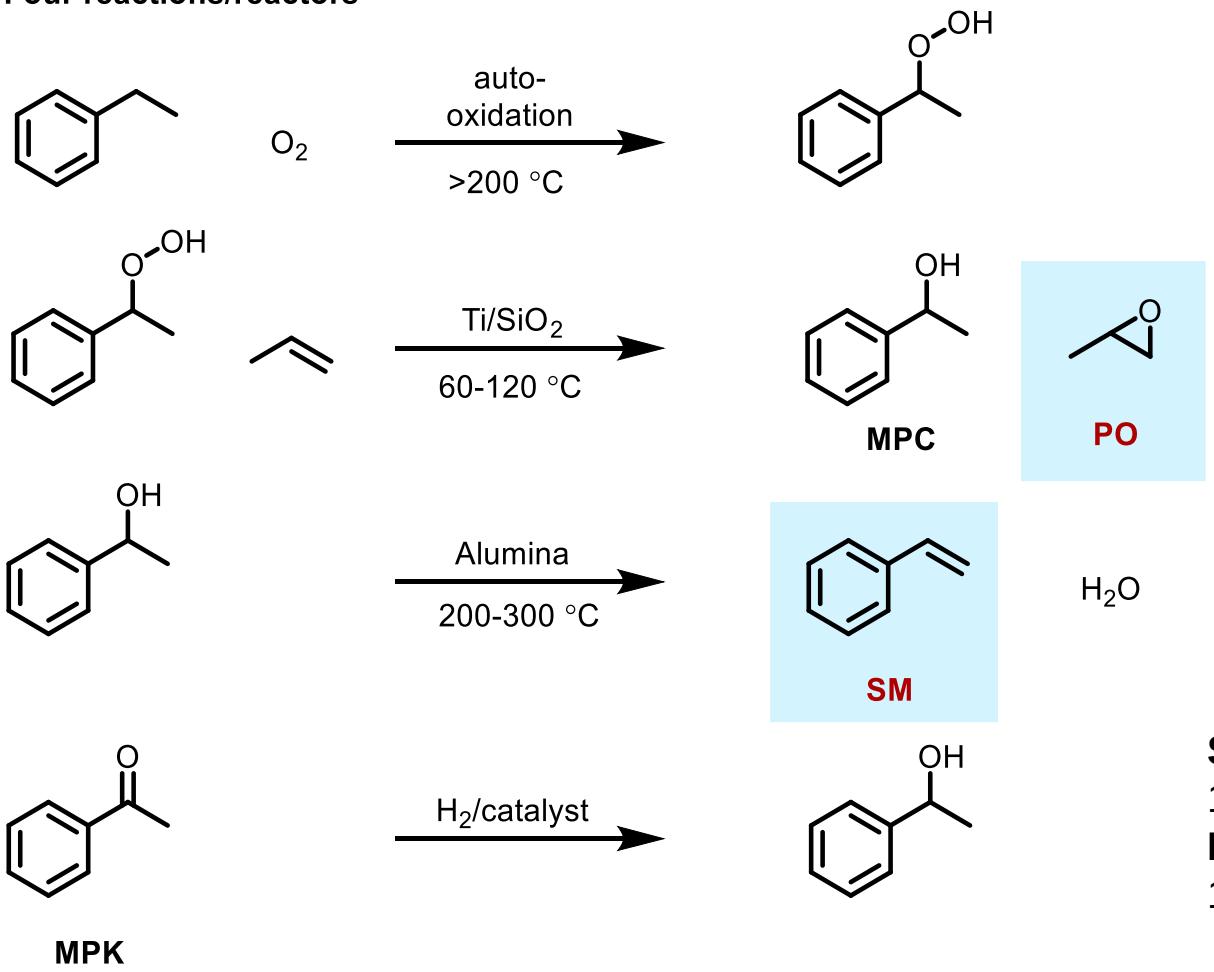


IBPO Process
organic molecule = isobutane
co-product = isobutene

SMPO Process
organic molecule = ethylbenzene
co-product = styrene monomer

- **Shell's SMPO Process**

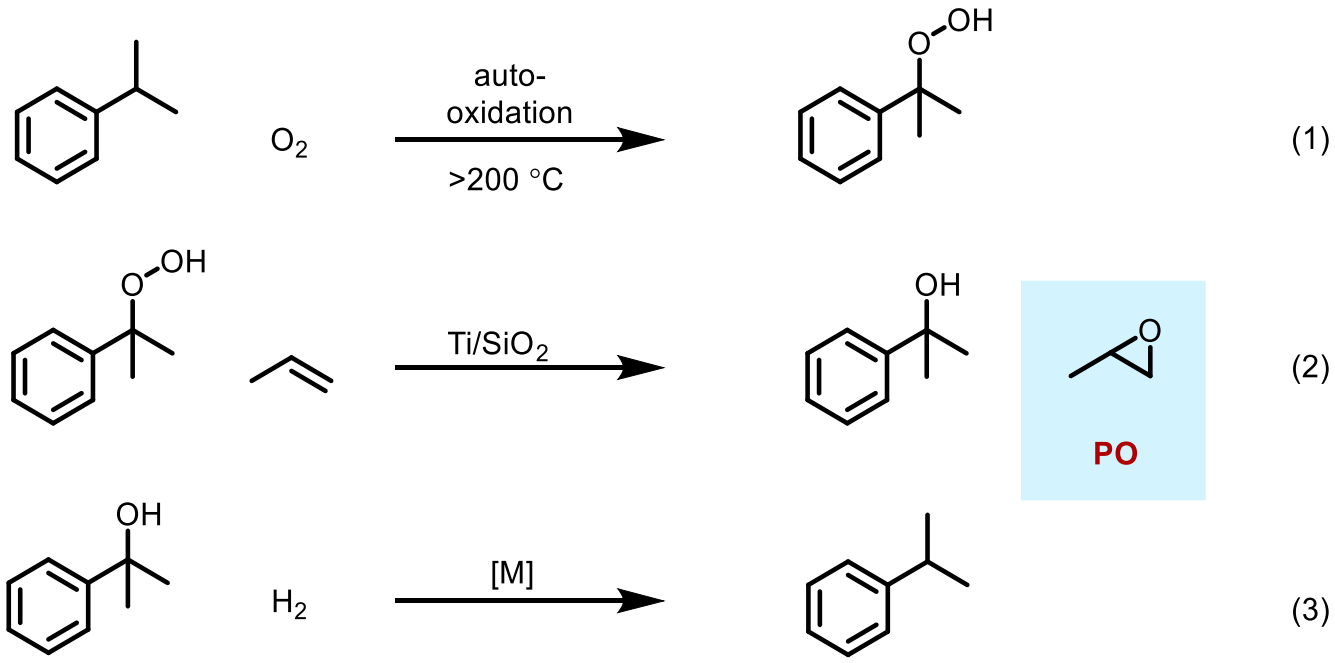
Four reactions/reactors



SMPO Process:
1 ton PO = 2.5 ton SM
IBPO Process:
1 ton PO = 2.1 ton IB

- **Sumitomo PO-only Process**

2000 Bench test
2001 Pilot testing
2002 Plant completion
2003 Plant startup

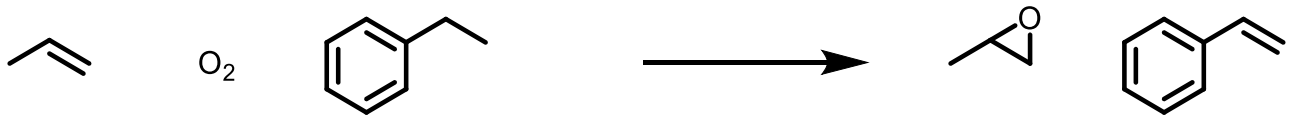


- Easier auto-oxidation in (1)
- Faster epoxidation in (2), 7 fold as SMPO process
- Exothermic epoxidation and hydrogenation, heat recovery
- Key of economy: cumene loss

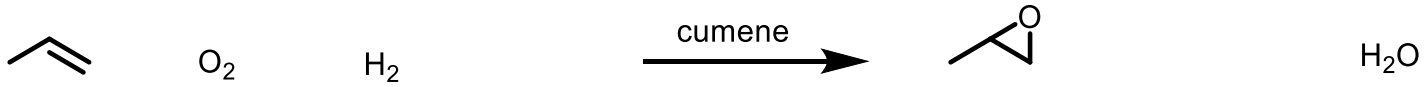
Sumitomo Kagaku, **2006**, *I*.

P450 Process

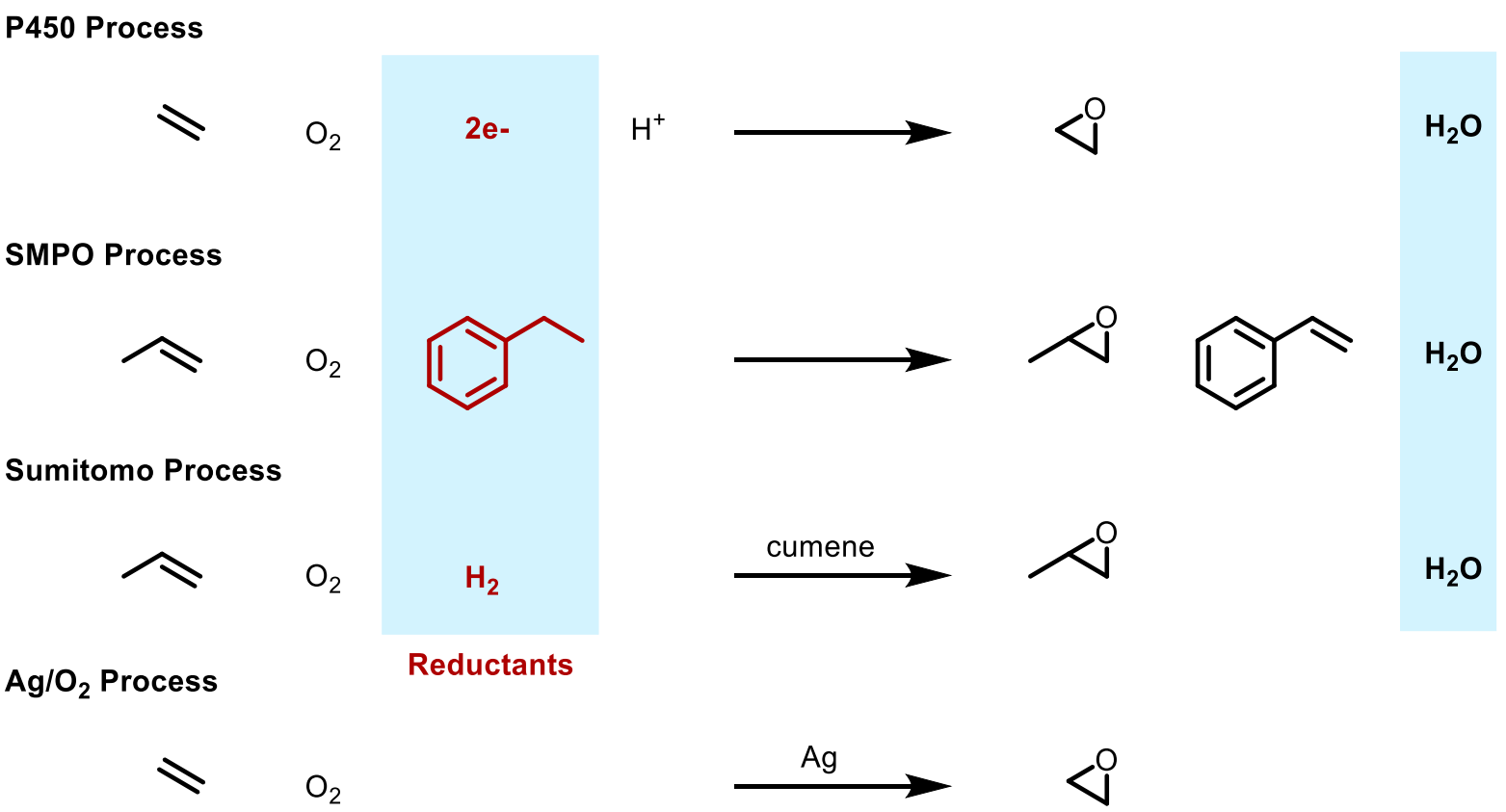
SMPO Process



Sumitomo Process



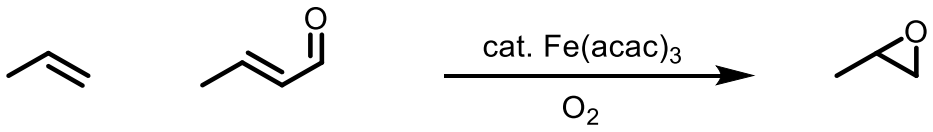
Ag/O_2 Process



- EB and hydrogen as **artificial NAD(P)H**
- Ag/oxygen system closer to ideal, but needs high temp, lacks selectivity and scope

Aldehydes as coreductants

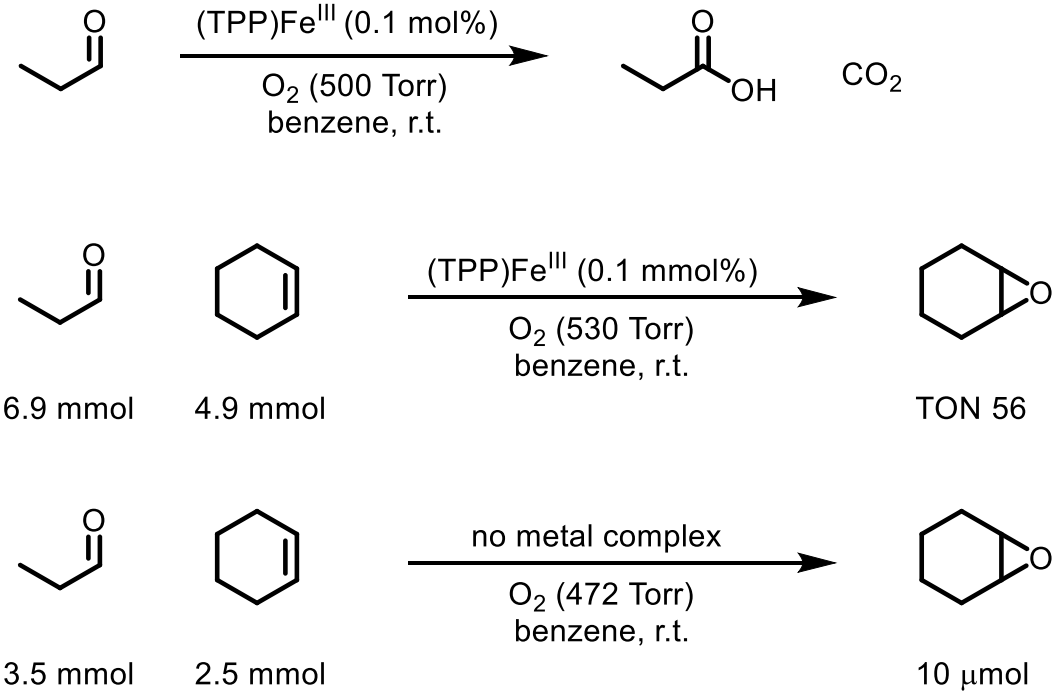
- Untraceable chemistry
  - **Pr(OAc)8** catalyzed aerobic epoxidation of olefinic compounds (e.g. terpenes) in the coexistence of aldehydes (1984)
  - **Fe(III)** catalyzed aerobic epoxidation of propylene with aldehdyes

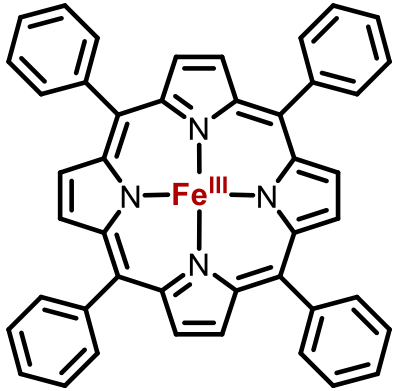


JP Patent 59-231077, **1984**
Kogyo Kagaku Zasshi, **1970**, *73*, 99.

Aldehydes as coreductants

- Early discovery





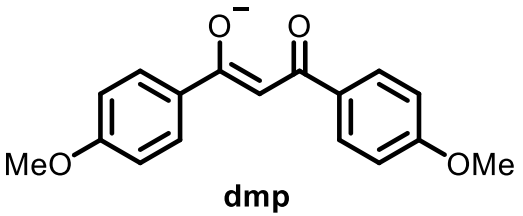
(TPP)Fe^{III}

- Peroxy acid proposed as intermediate
- Peracid decarboxylation by P450 is known

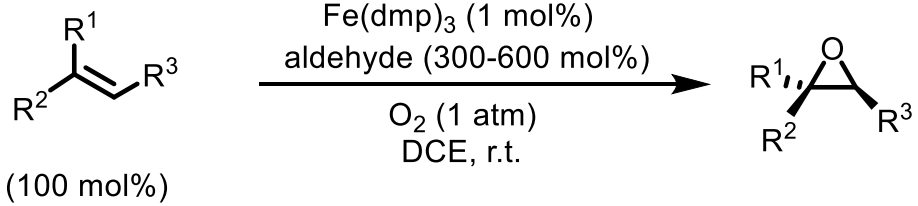
J. Chem. Soc., Chem. Commun., **1990**, 1323.

Aldehydes as coreductants

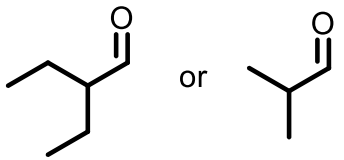
- Systematic study of scope



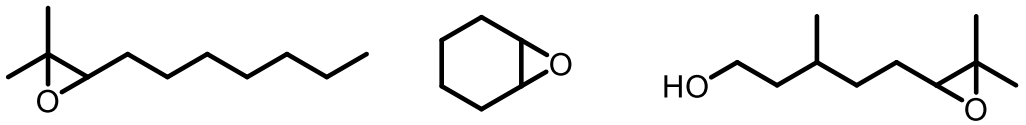
dmp



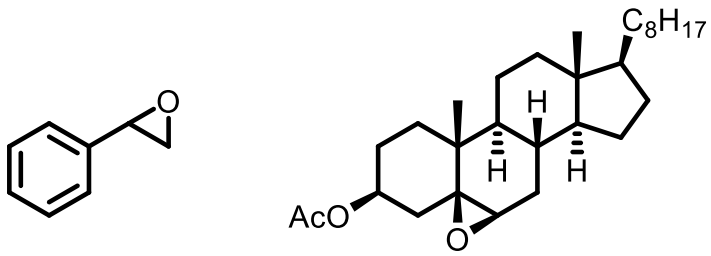
aldehyde:



Selected examples:



Quant. 80% Quant.

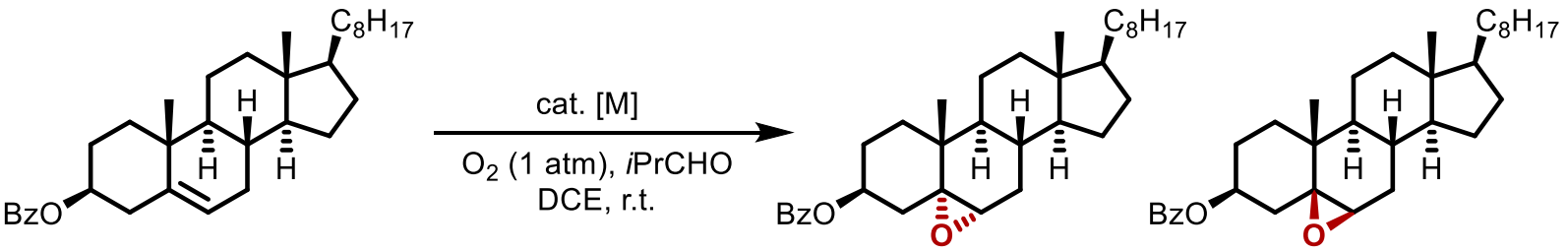


89% 86%

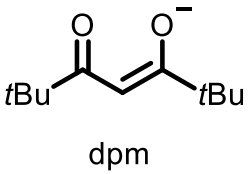
Bull. Chem. Soc. Jpn., **1991**, *64*, 2513.

Aldehydes as coreductants

- Versatile system



α-epoxide β-epoxide



dpm

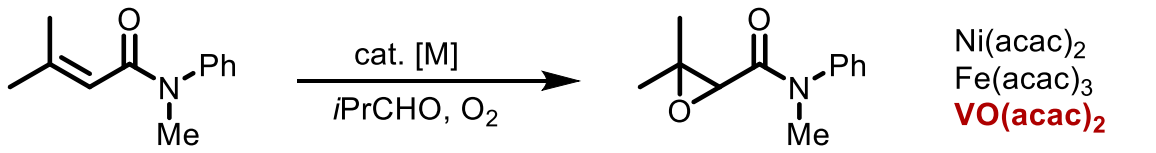
$Ni(dmp)_2$	31	69	
$Fe(acac)_3$	33	67	
$Pd(acac)_2$	30	70	
$Ru(acac)_3$	24	76	
$Co(acac)_2$	23	77	
$Mn(acac)_2$	20	80	
$Mn(dpm)_2$	**18**	**82**	93% Yield
***m*-CPBA**	**71**	**29**	

- Suitable system for a wide range of metals
- Metal complex does play a role

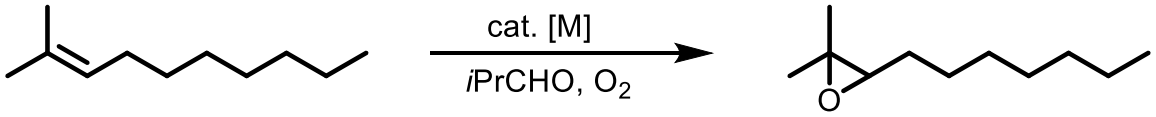
Chem. Lett., **1992**, 2109.

Aldehydes as coreductants

- Vanadium: complementary scope



	Yield (%)
$Ni(acac)_2$	trace
$Fe(acac)_3$	26
$VO(acac)_2$	**71**



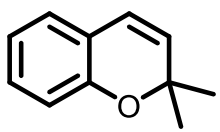
	Yield (%)
$Ni(acac)_2$	Quant.
$VO(acac)_2$	**0**

- Coordination of amide might be the key

Chem. Lett., **1991**, 941.

Aldehydes as coreductants

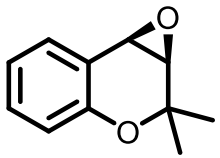
- Enantioselective epoxidation



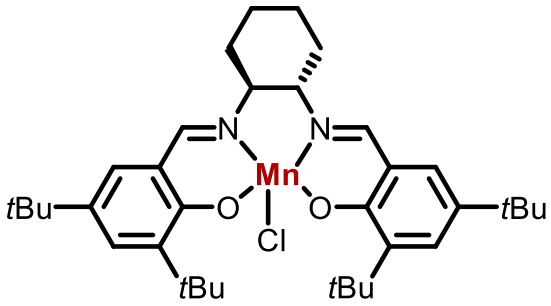
(100 mol%)

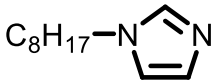
Mn(III) (12 mol%)

*t*BuCHO (300 mol%)
NAI (50 mol%)
O_2 (1 atm)
benzene, 25 °C



37% Yield
92% *ee*



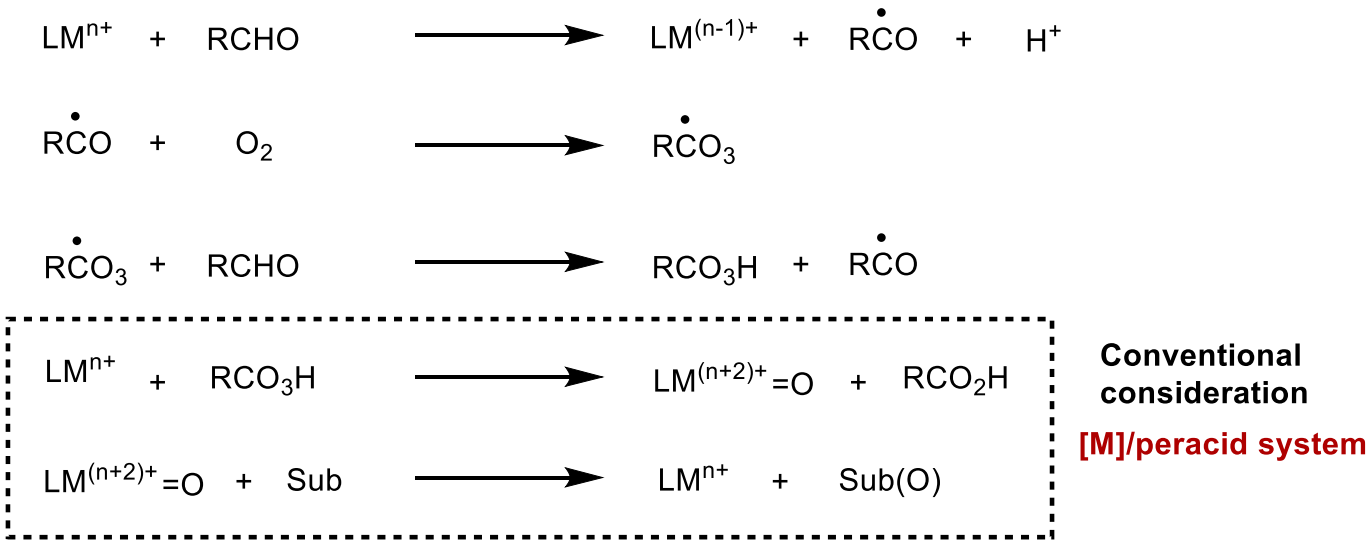
NAI: 

Chem. Lett., **1992**, 2231.

Aldehydes as coreductants

- Mechanistic consideration

What's the true oxidizing reagent?



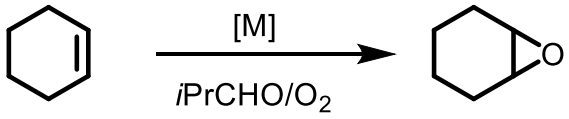
Candidates:

$LM^{(n+2)+}=O$ $\quad$ $R\dot{C}O_3$ $\quad$ RCO_3H

Chem. Lett., **1992**, 2231.

Aldehydes as coreductants

- Study of model reaction



3 mmol

	(mmol)
Cr(TPP)Cl	1.0
Mn(TPP)Cl	1.0
Fe(TPP)Cl	1.0
Co(TPP)	1.0
Co(TPP)+radical inhibitor	**0.0**
Ni(TPP)	1.2
Cu(TPP)	0.2
Zn(TPP)	0.0
no metal	**0.6**

Candidates:

$LM^{(n+2)+}=O$ $R\dot{C}O_3$ RCO_3H

- Metal-oxo not likely
- Involving radical pathway

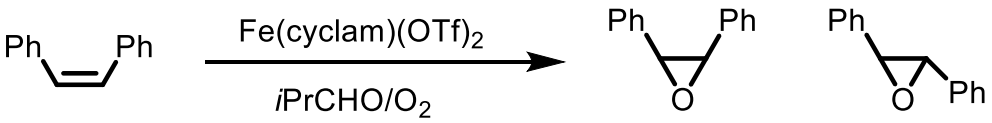
Chem. Lett., **1992**, 2231.

Aldehydes as coreductants

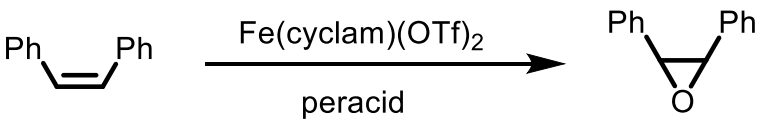
- Stilbene experiments

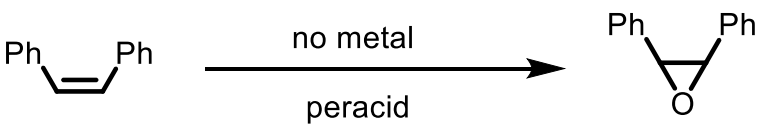
Candidates:

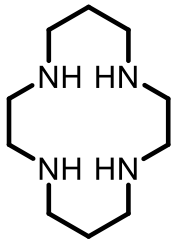
$LM^{(n+2)+}=O$ $\quad$ $R\dot{C}O_3$ $\quad$ RCO_3H



cis:trans = 0.26







cyclam

- Metal-oxo not likely
- Solely peracid not likely
- Acylperoxy radical more plausible

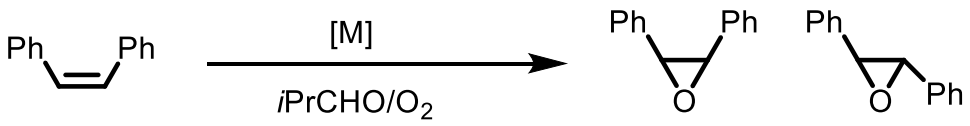
Chem. Lett., **1992**, 2231.

Aldehydes as coreductants

- Stilbene experiments

Candidates:

$LM^{(n+2)+}=O$ $\quad$ $R\dot{C}O_3$ $\quad$ RCO_3H



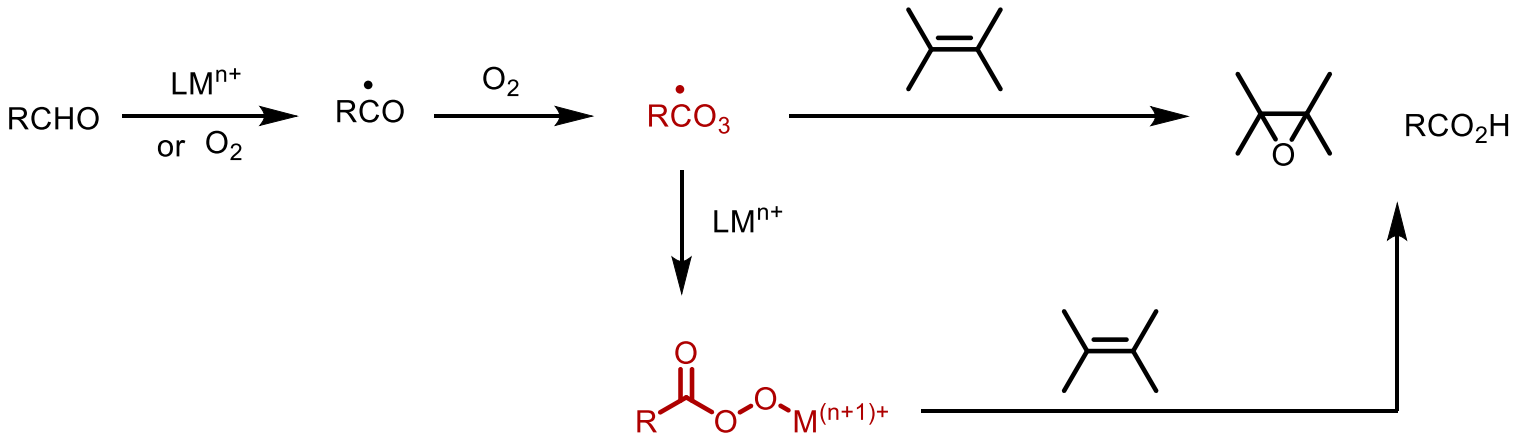
	cis:trans
Cr(TPP)Cl	0.28
Mn(TPP)Cl	0.88
Fe(TPP)Cl	0.30
Co(TPP)	0.28
Ni(TPP)	0.30
$Mn(cyclam)^{2+}$	0.91
$Fe(cyclam)^{2+}$	0.23
$Co(cyclam)^{2+}$	0.21
$Cu(cyclam)^{2+}$	0.26

- Might have two pathways

Chem. Lett., **1992**, 2231.

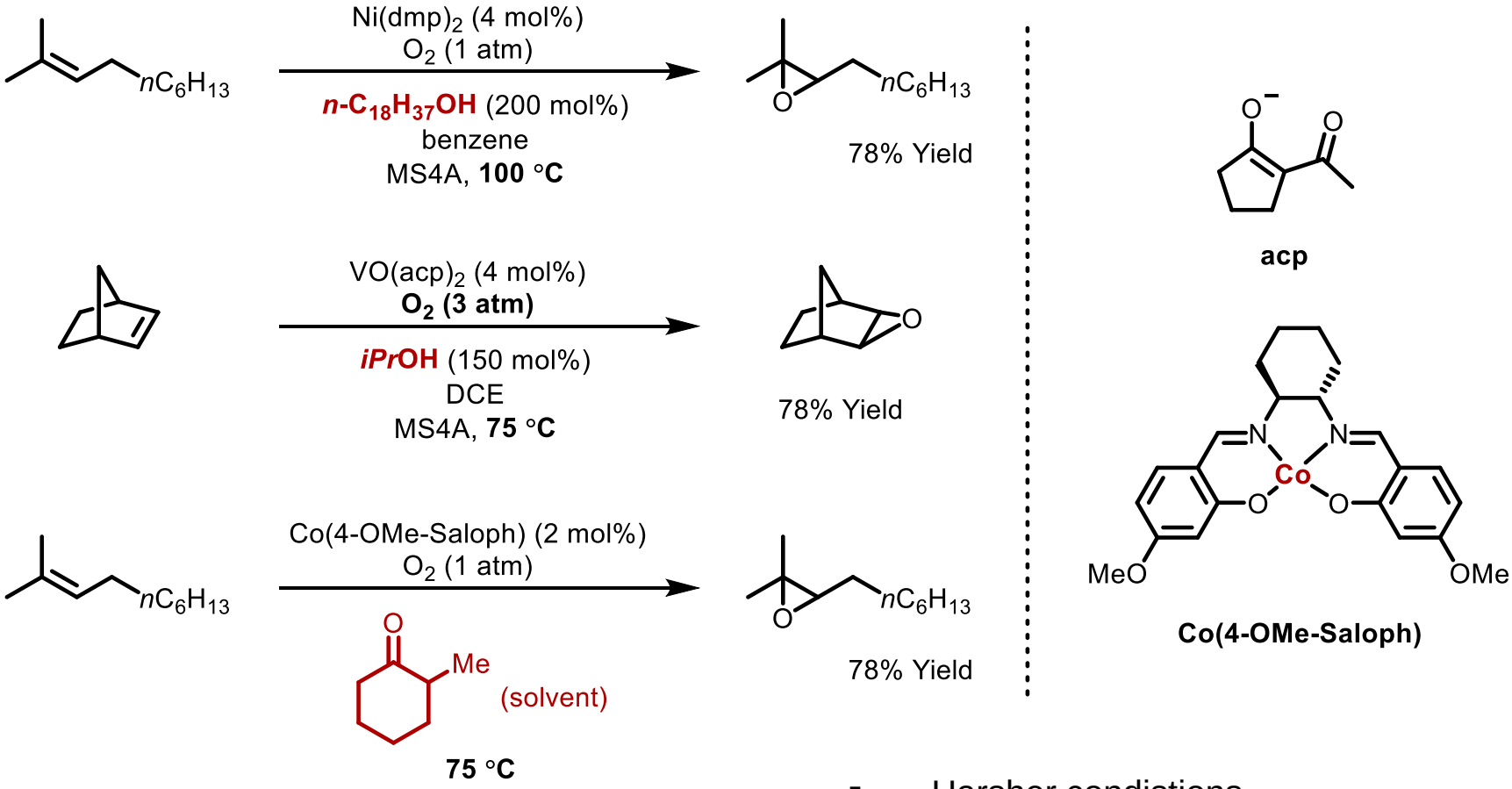
Aldehydes as coreductants

- Proposed pathways



Inorg. Chem., **1996**, *35*, 1045.

Other coreductants



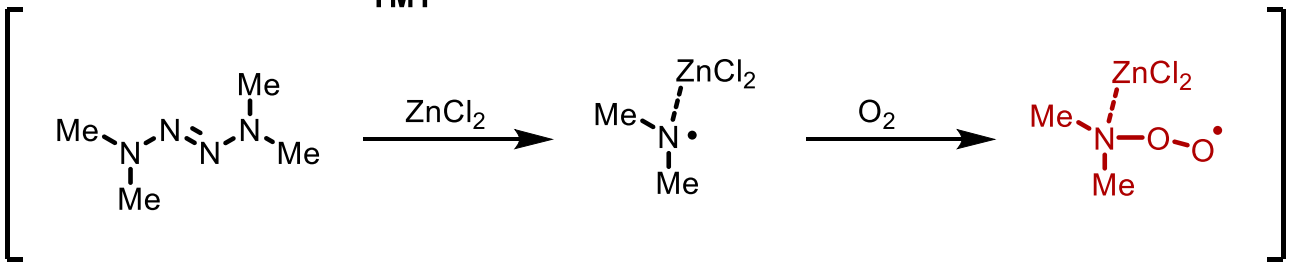
- Harsher condistions
- Alfa-hydroxy ketones observed

Chem. Lett., **1990**, 1661.
Chem. Lett., **1990**, 1657.
Chem. Lett., **1992**, 2077.

Interesting Pd/azibenzil system

Precedent

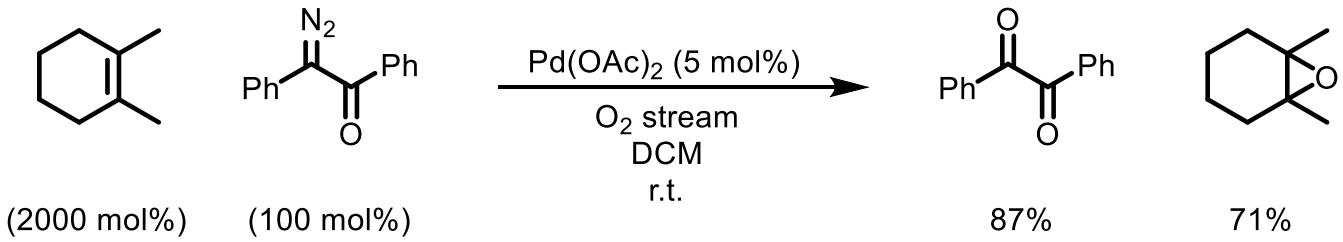
TMT



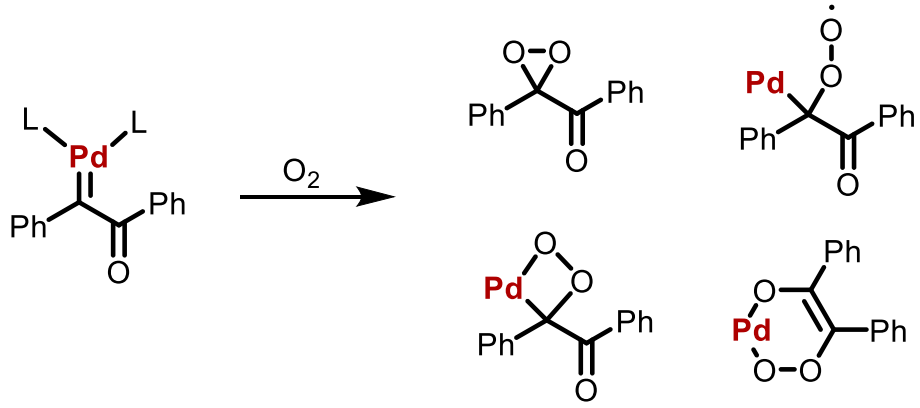
- Details not available
- Likely stoichiometric in TMT

JACS, **1976**, *98*, 6728.

Interesting Pd/azibenzil system

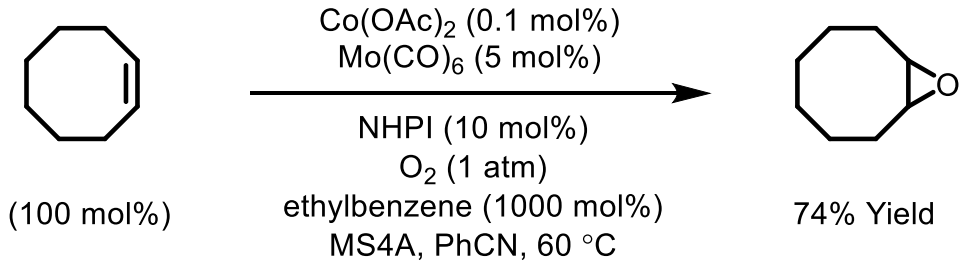


possible active species



JACS, **1980**, *102*, 2129.

A homogeneous analogue to SMPO process



Recap on SMPO

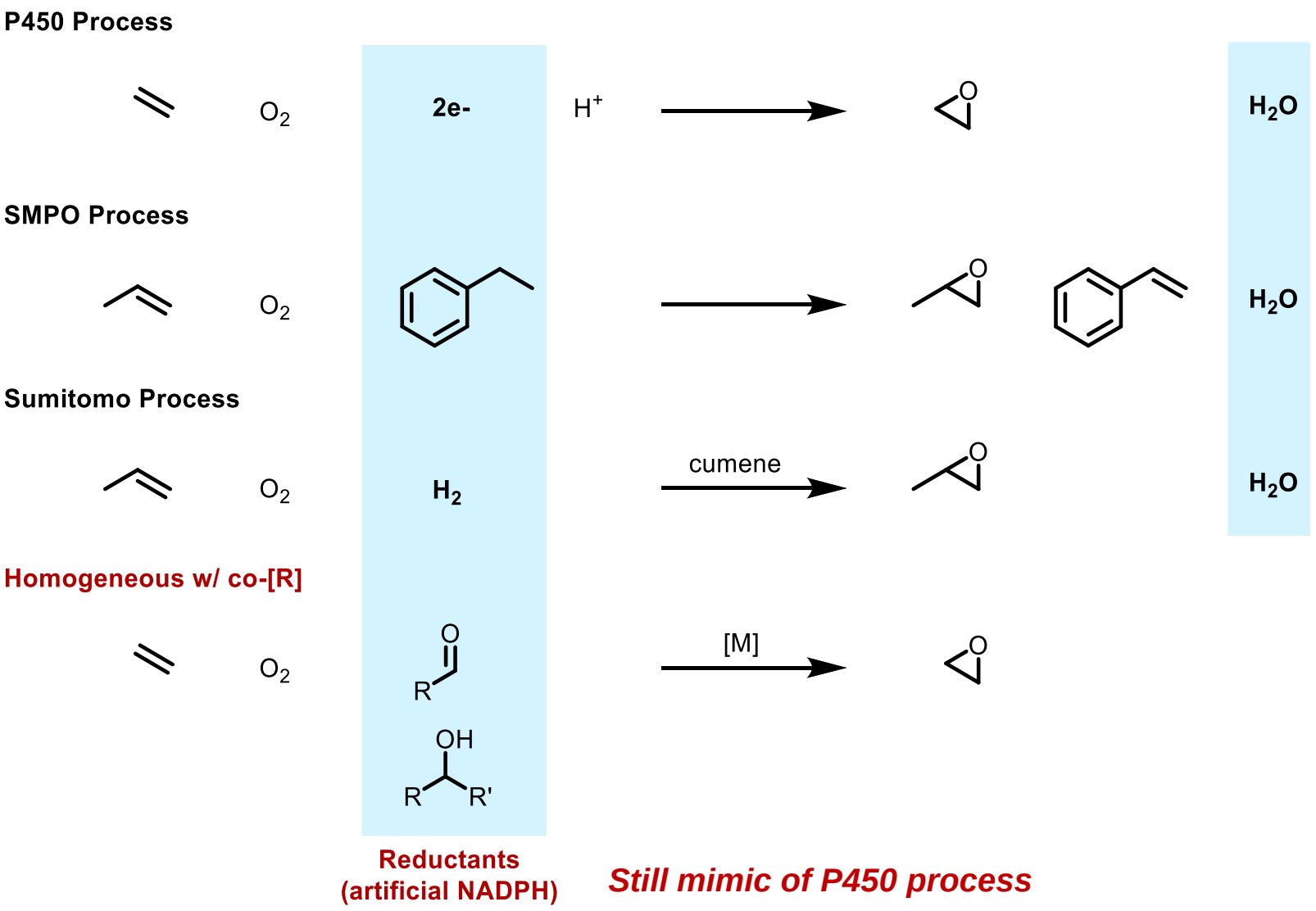
- Auto-oxidation of EB: high T, high pressure
- Generation of organic peroxide
- Ti-catalyzed epoxidation

This version

- Mo-catalyzed epoxidation
- Co(II) can be easily oxidized by O2 to Co(III)
- Auto-oxidation assisted by NHPI

Ishii, *Chem. Commun.* **2000**, 163

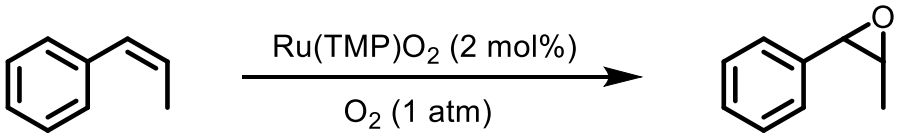
Comparison again



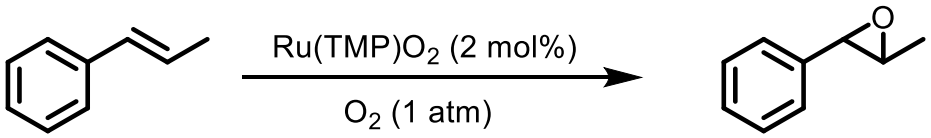
Without reductant

- Not fully understood
- Limited studies

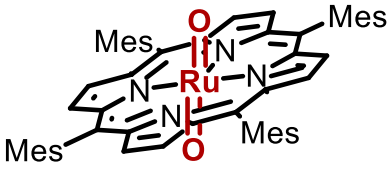
Groves' Ruthenium Porphyrin System

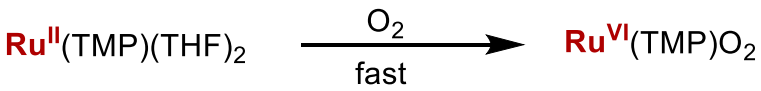


65% Yield



33% Yield



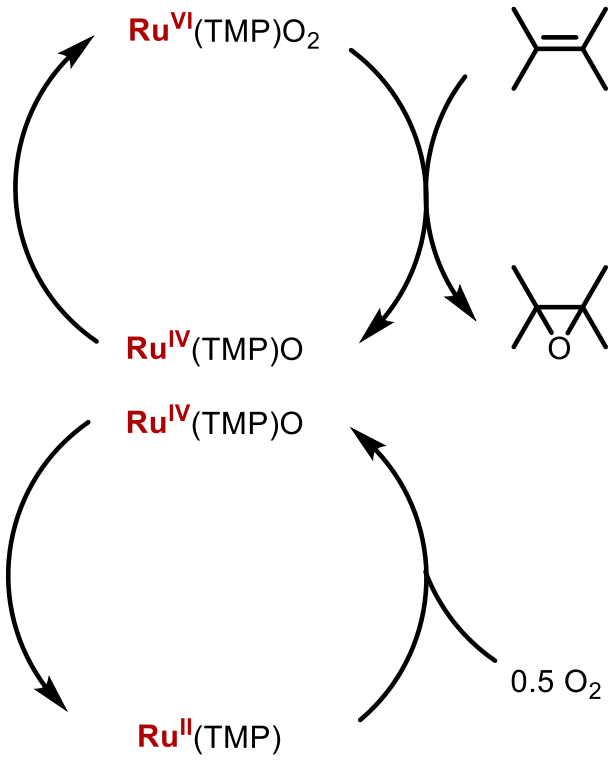


- Manometric: **2 mol epoxide formed = 1 mol oxygen**
- Ru(II)(TMP)(THF)2 can catalyze the reaction
- UV spectrum: little Ru(VI) and no Ru(II)

Ideal 'Dioxygenase'

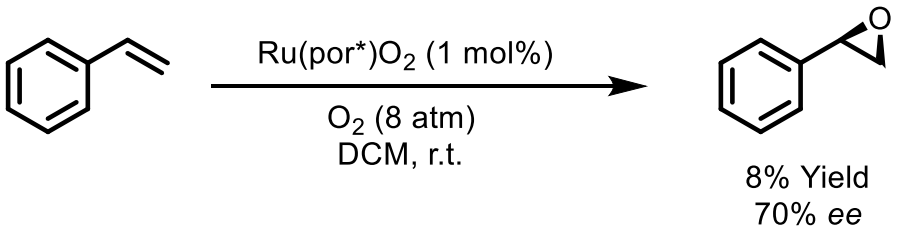
JACS, **1985**, *107*, 5790

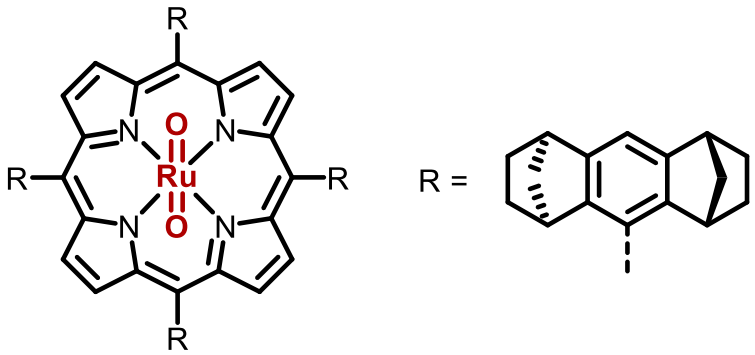
Groves' Ruthenium Porphyrin System



JACS, **1985**, *107*, 5790

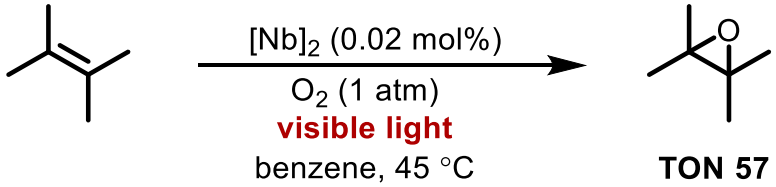
Enantioselective epoxidation using Ru(VI)



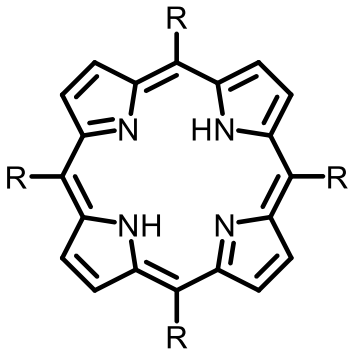


CC, **1998**, 1583

Niobium Porphyrin system

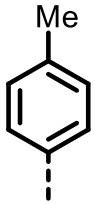


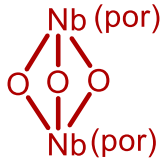
TON 57



porH$_2$

R =

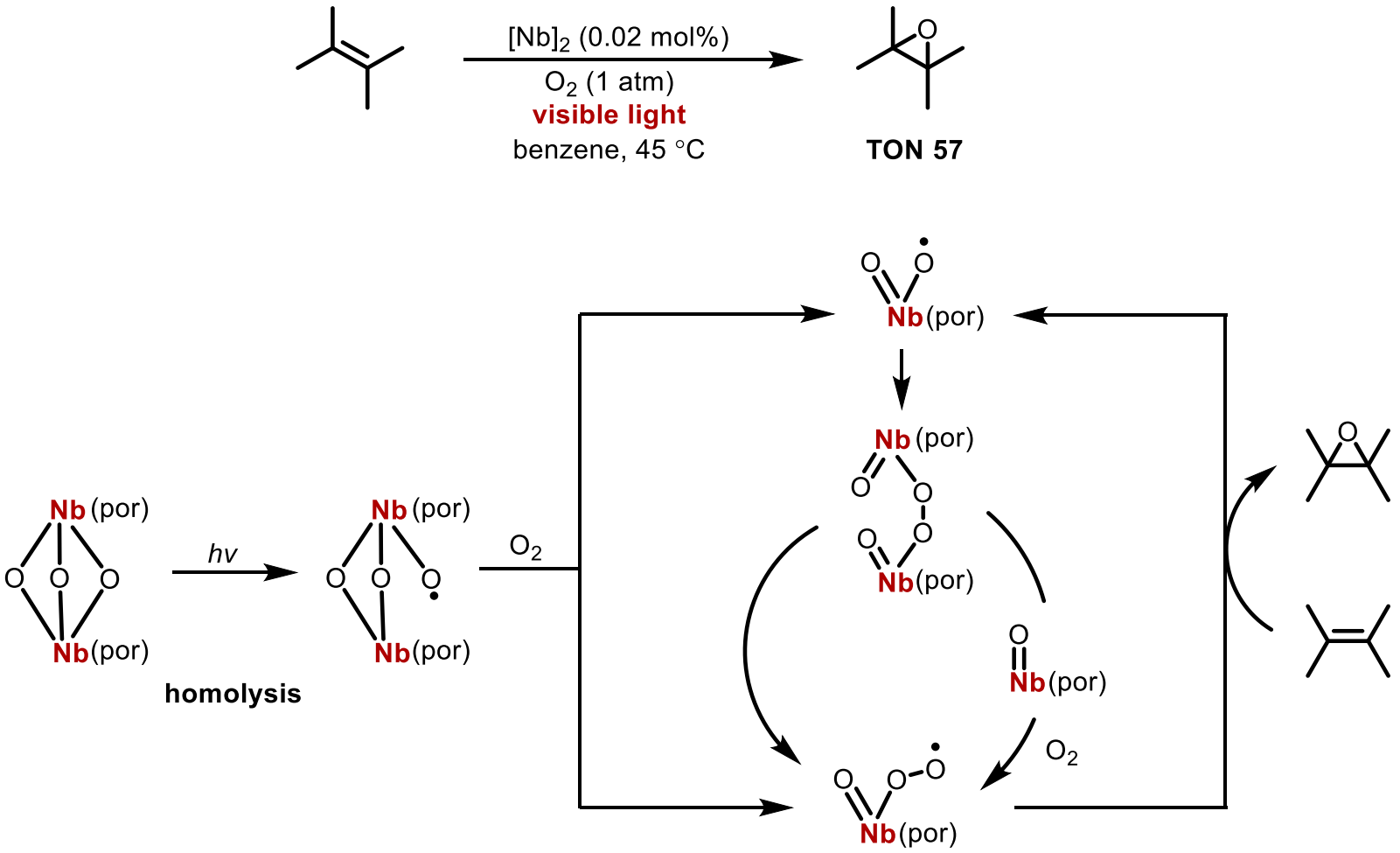




Nb(por) dimer

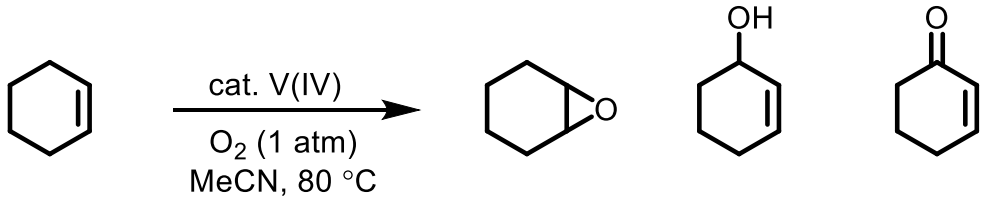
JACS, **1985**, *107*, 6416

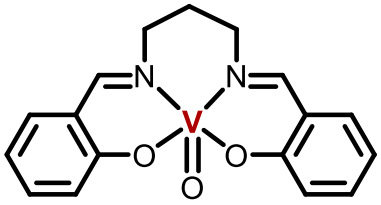
Niobium Porphyrin system



JACS, **1985**, *107*, 6416

V(IV)/V(V) system

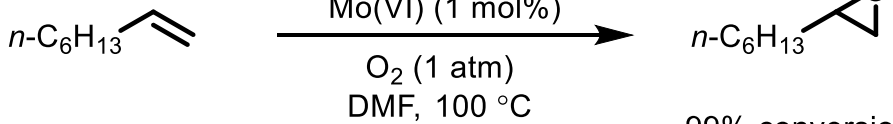


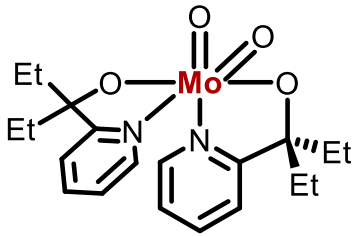


- Studies of ligand synthesis
- Smaller reduction potential of V(IV)/V(V), higher conversion
- Highest epoxidation selectivity 56%
- Cyclohexene as the only case, auto-oxidation not excluded

J. Mol. Catal. A, Chem. **2002**, 179, 41

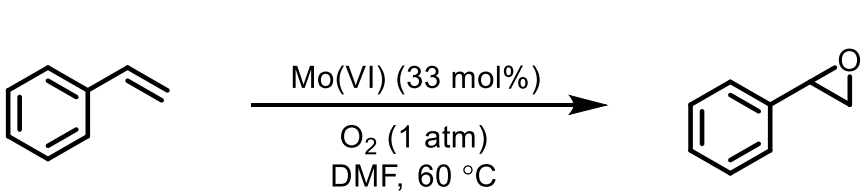
Dioxomolybdenum system

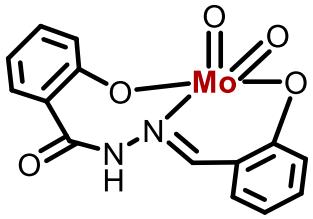




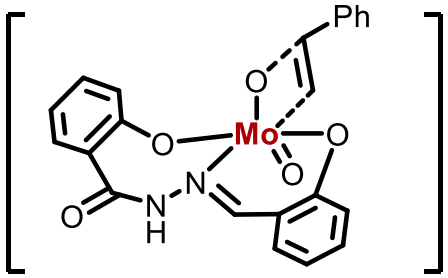
99% conversion
58% selectivity

no catalyst: 24% selectivity, conversion n.a.
MoO_3: 38% selectivity, conversion n.a.
$MoO_2(acac)_2$: 6.9% selectivity, conversion n.a.





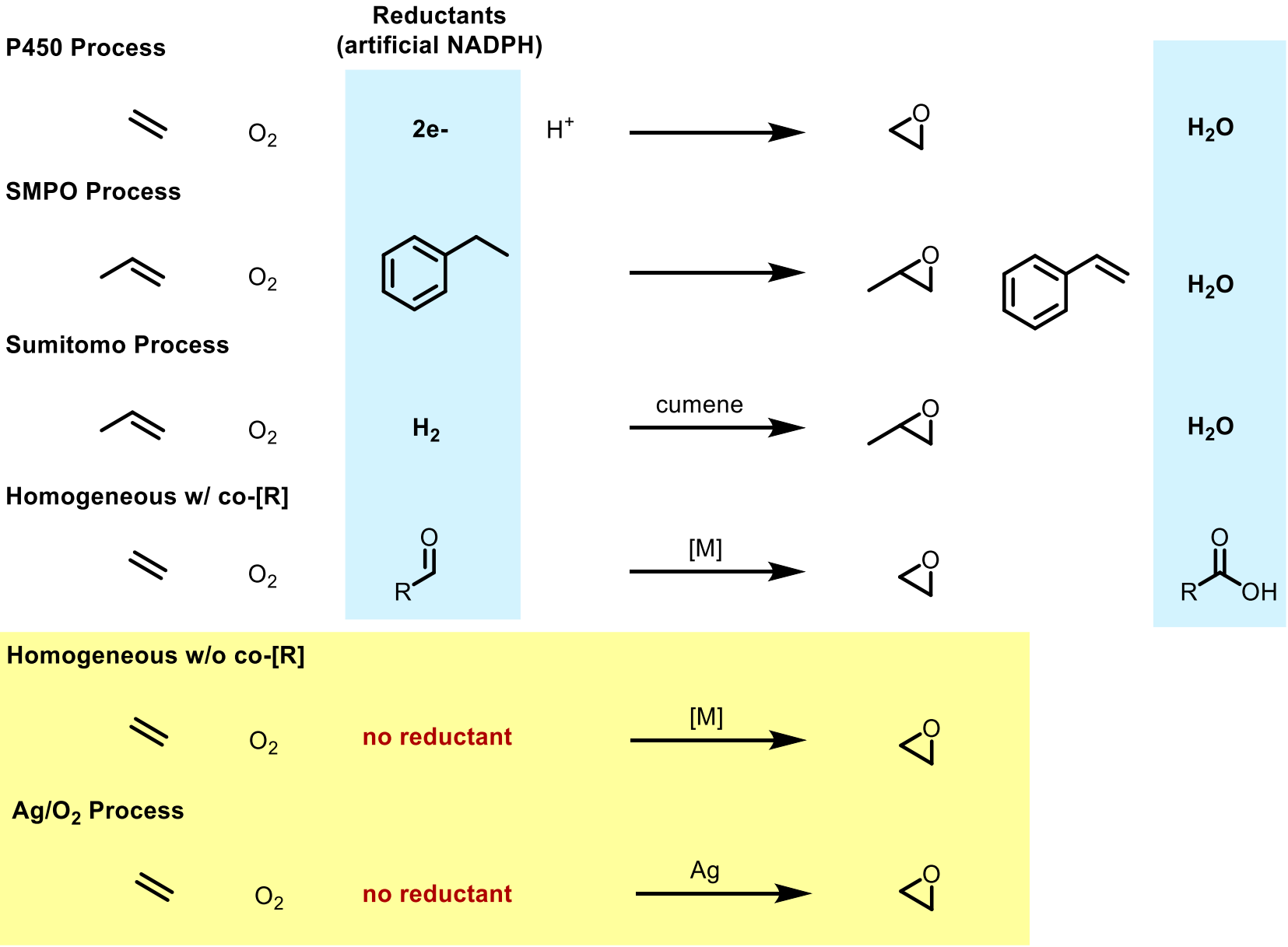
77% conversion
85% selectivity



Proposed intermediate

J. Mol. Catal. A, Chem. **2000**, 156, 205
J. Mol. Catal. A, Chem. **1997**, 117, 455
RSC Advance. **2012**, *2*, 8071

Comparison again



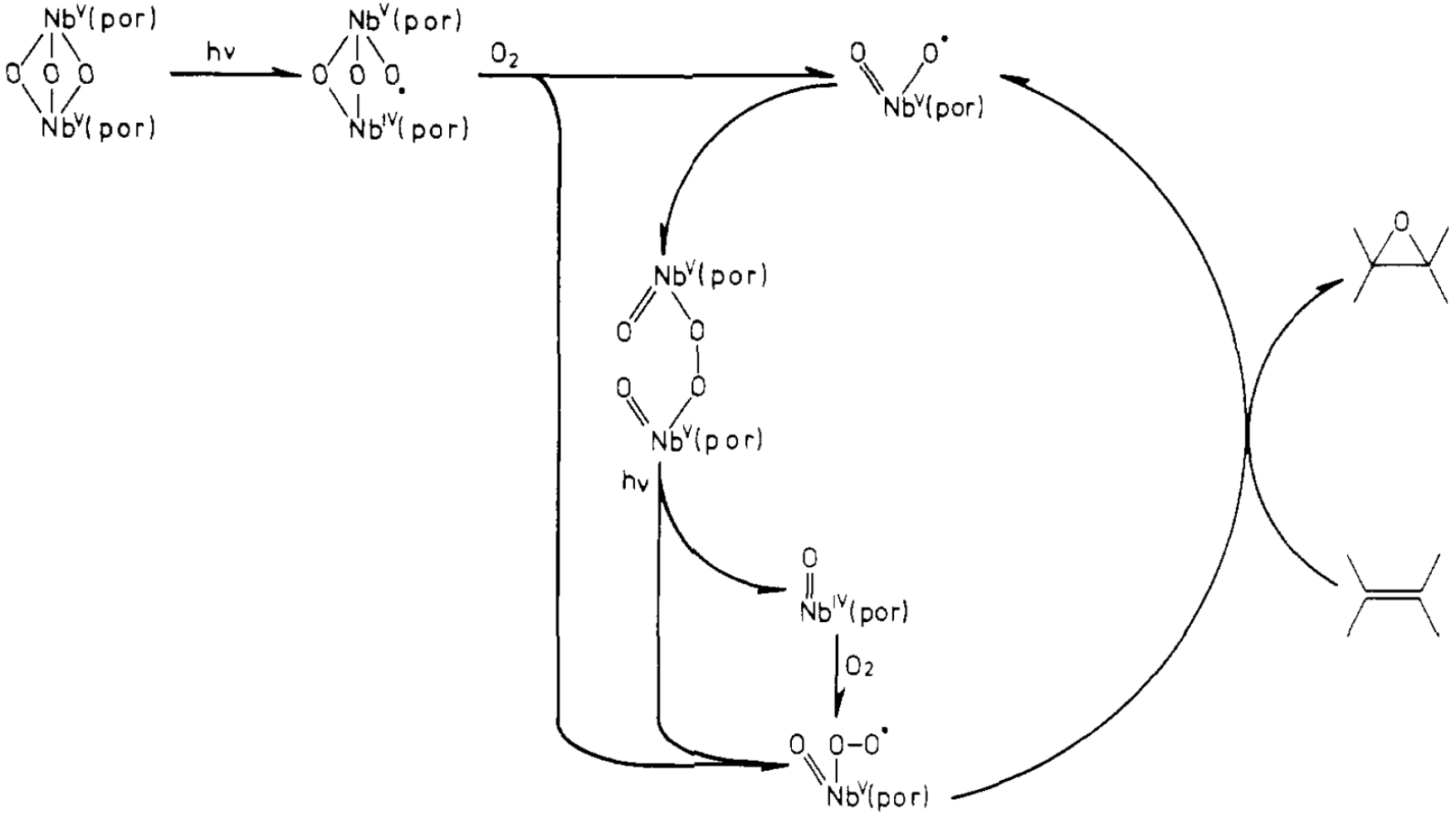
For Homogeneous catalysis

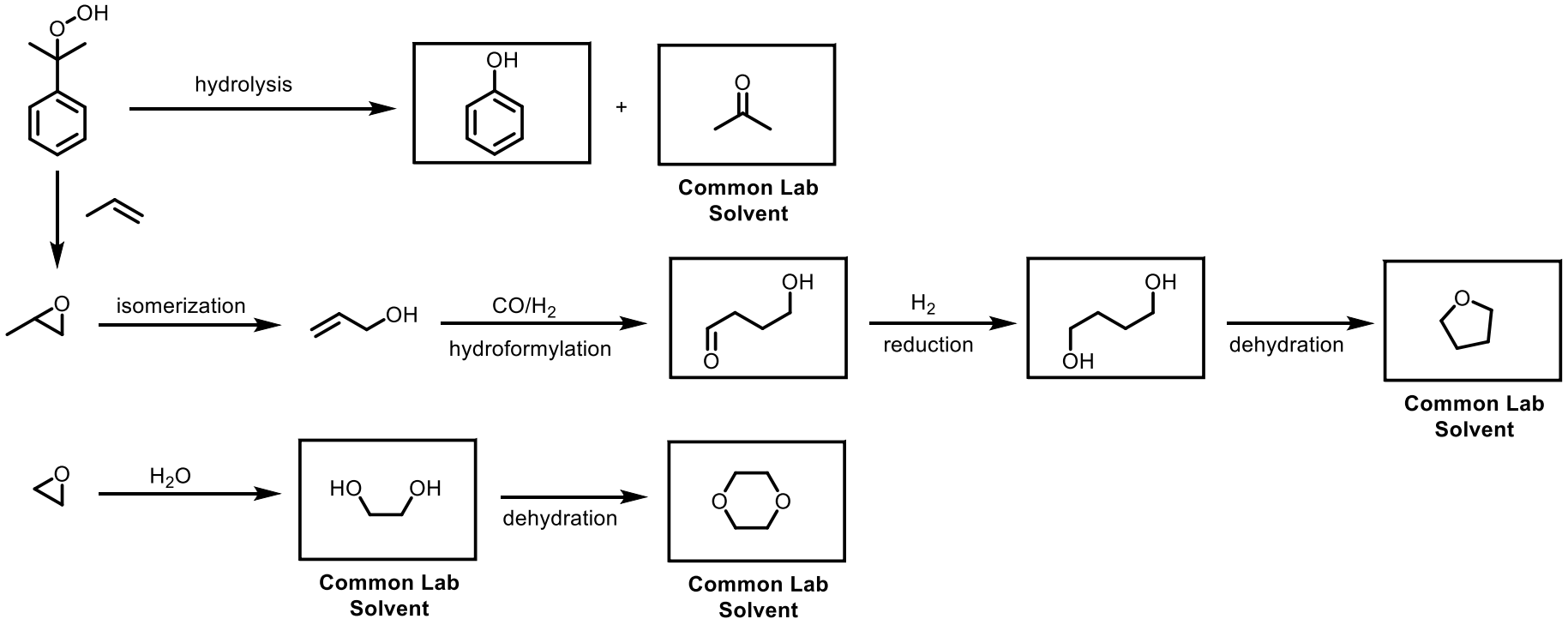
- High-valent di-oxometal complexes are promising
- Scope, compatibility and limitation needs to be studied

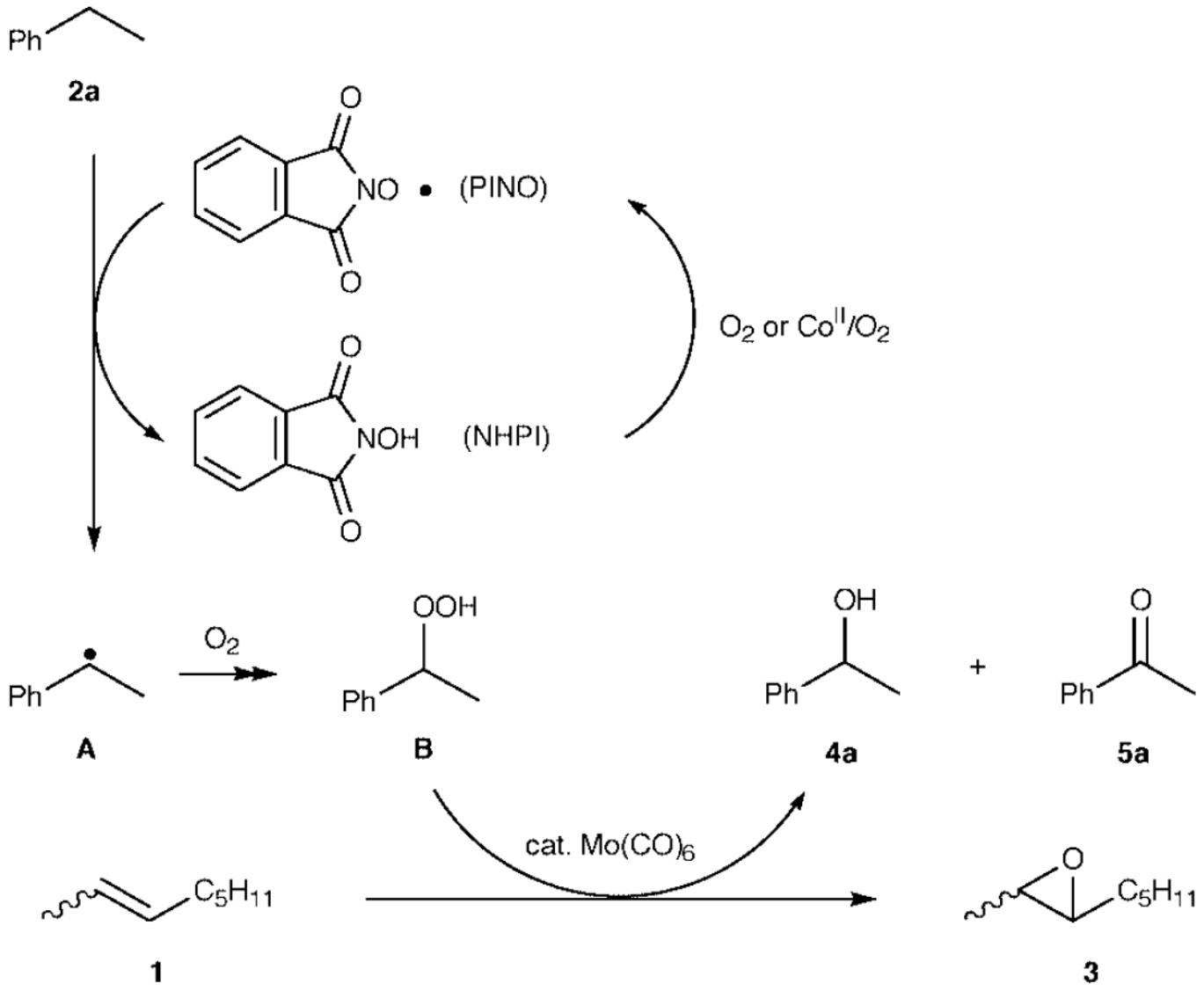
For Hetergeneous catalysis

- Issues of temperatures and selectivity still need to be addressed
- When will Ag/O2 process be phased out?
- New form of catalysis?
- Next generation method should be mild, energy-saving and universal


Thank
you!


Nb^V(por)
hν
Nb^V(por)
Nb^IV(por)
O2
Nb^V(por)
Nb^V(por)
Nb^V(por)
hν
Nb^IV(por)
O2
O–O
Nb^V(por)


OH
O
hydrolysis
OH
+
O
Common Lab Solvent
O
isomerization
OH
CO/H2
hydroformylation
OH
O
H2
reduction
OH
OH
dehydration
O
Common Lab Solvent
O
H2O
HO
OH
Common Lab Solvent
dehydration
O
O
Common Lab Solvent


Ph
2a
O
NO •
(PINO)
O
O
NOH
(NHPI)
O
O2 or Co^II/O2
Ph
A
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OOH
Ph
B
OH
Ph
4a
+
O
Ph
5a
cat. Mo(CO)6
C5H11
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C5H11
3