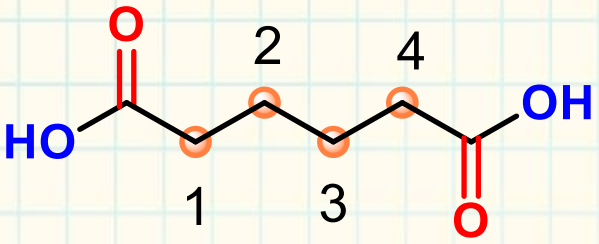
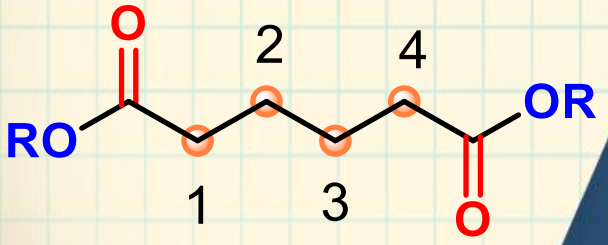




Routes to adipic acid (esters)

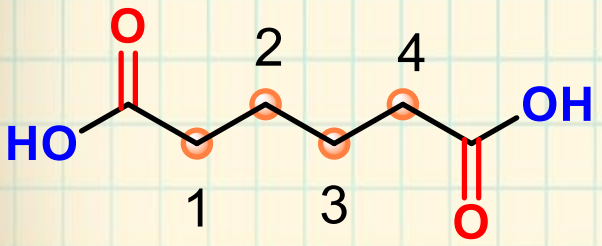
—— Carbonylation of 1,3-butadiene

Reporter： Meng Wang

Supervisor: Dr. Ping Lu

2020.06.18

Contents



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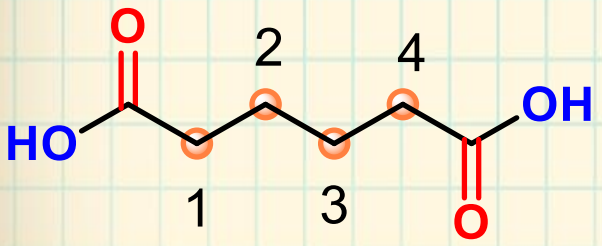


Industry status

Global adipic acid demand

- Over 2.7 million metric tons
- growing at 3–5% per year
- Over 4.6 billion US dollars

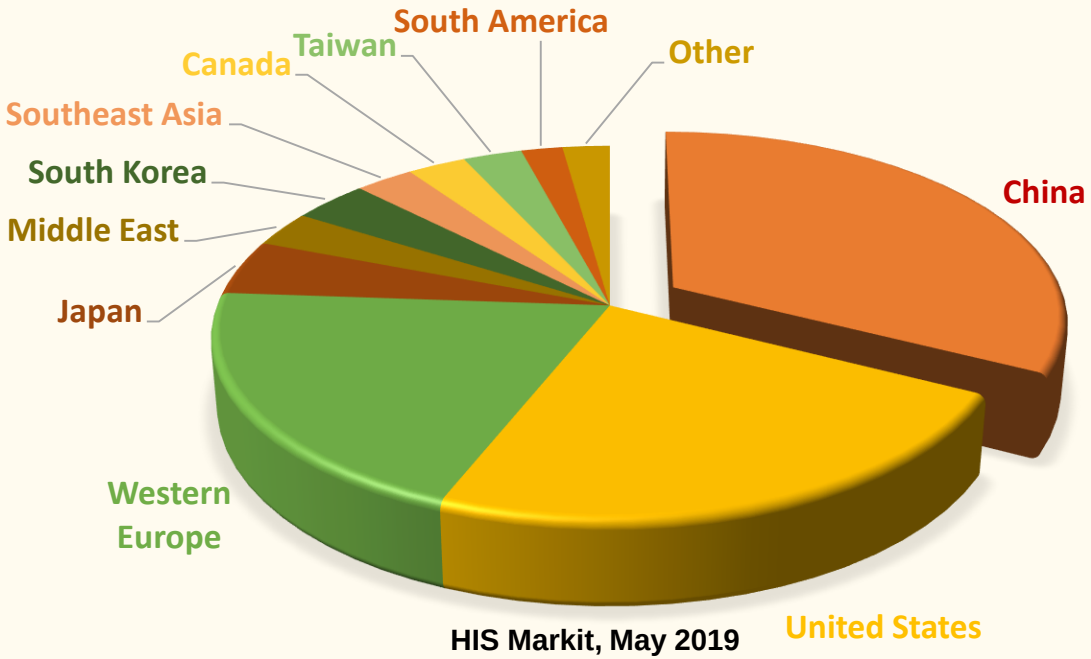
Asia adipic acid demand

- 45–55% of global consumption
- growing at 4.7% per year

China adipic acid demand

- 30% of global consumption
- growing at 6% per year

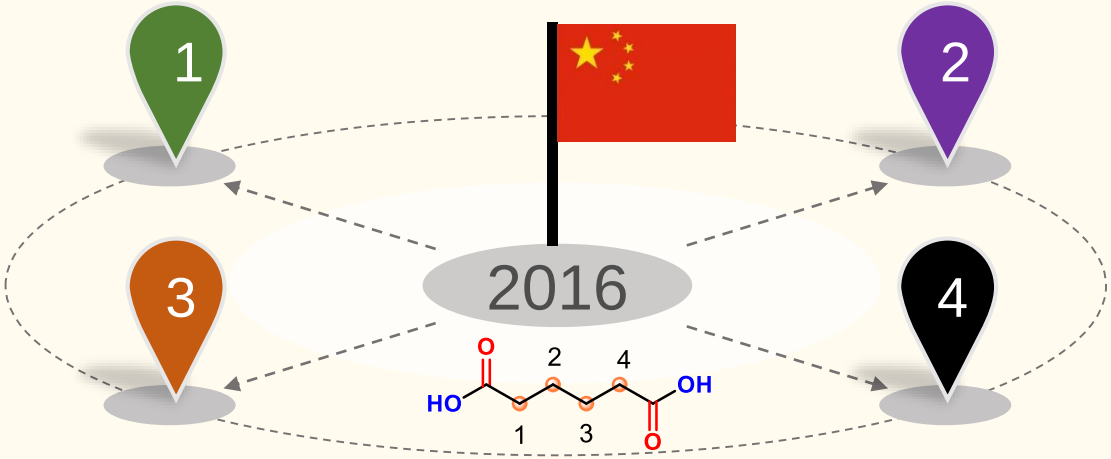
World Consumption Of Adipic Acid (2018)



In terms of magnitude and growth, China leads the pack

total global capacity
~ 50%

global production
40%



global consumption
30%

global export market
> 50%

HIS Markit, May 2019

Adipic acid is used for?

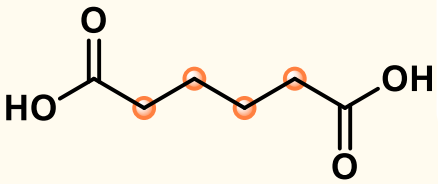
Nylon

Polyurethanes

Plasticizers

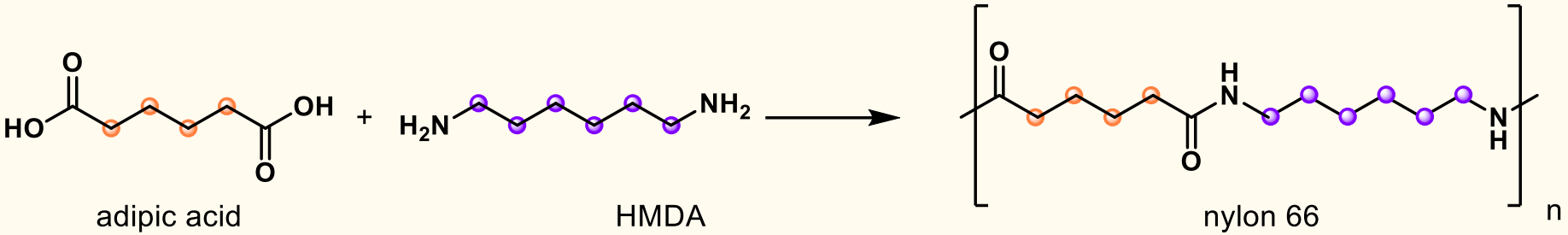
Food additives:
Gelling agents
Flavor ants

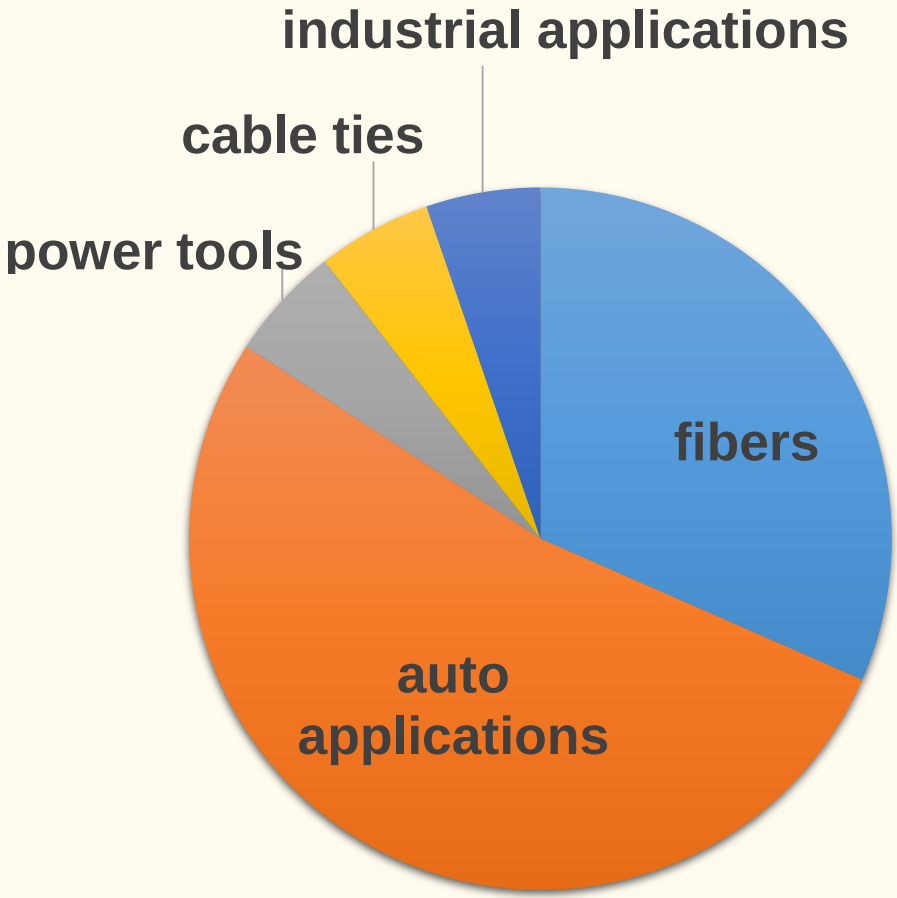
Other products:
Paper additives
Cosmetics
Lubricants
Pharmaceuticals



adipic acid

The major market: a feedstock for nylon 66



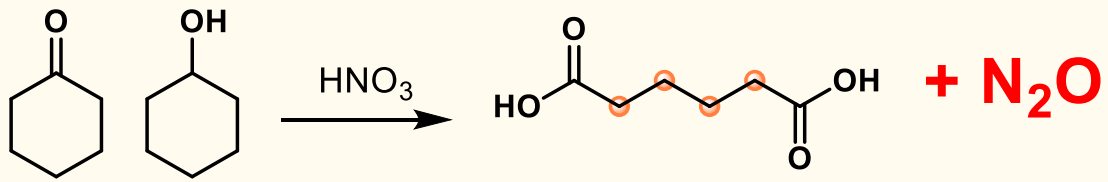


Nylon 66 will be the fastest-growing market for adipic acid in the forecasting period.

October 8, **2018** C&EN, Alex Tullo

Problems existing in conventional way

N_2O, laughing gas
popular drug among 16~24 age group



KA oil

adipic acid

N_2O

safety concerns

large investment

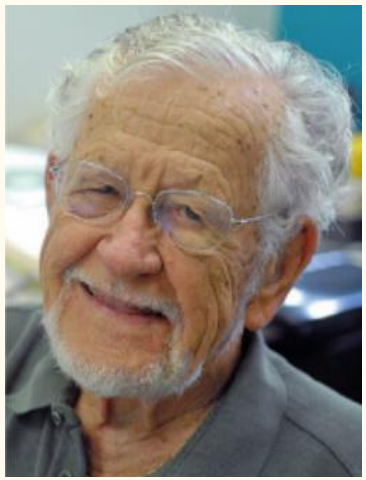
equipment corrosion

M. H. Thiemens, W. C. Trogler, *Science* **1991**, *251*, 932

Barton Challenge: Adipic acid from n-hexane

——by Roberts, In Feb. 1998

Derek H. R. Barton
8 Sep. 1918 ~ 16 Mar. 1998

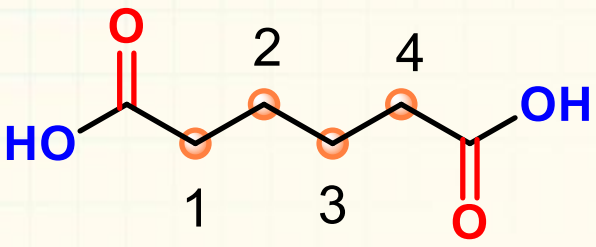


John D. Roberts
8 Jun. 1918 ~ 19 Oct. 2016

Purpose	In honor of Barton's groundbreaking research in selective oxidation of aliphatic and alicyclic hydrocarbons
Award	**$5,000**
Content	the first person or research group to produce adipic acid by a chemical or biochemical oxidation hexane with an 85% yield on the basis of hexane consumed

- Many chemists thought the person best suited to meet the Barton Challenge was Barton himself.
- But Barton, died March 16, 1998.
- On the day of Barton's death," Roberts says, "I received a letter from him and, with respect to the challenge, he wrote: 'The competition prize will probably escape me in this world. I will work on it in heaven where time is infinite.' "

Contents

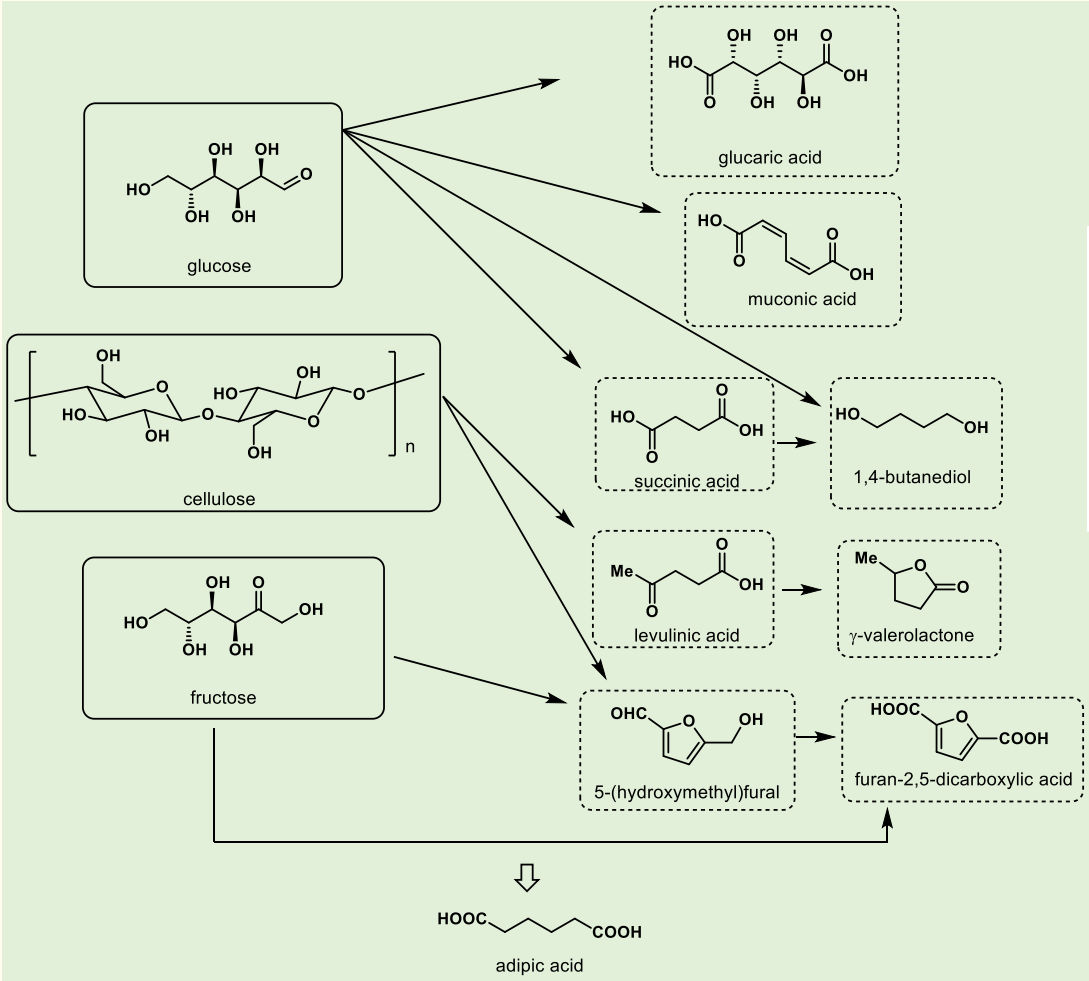


- **The bio-based routes**
- **The petrochemical-based routes**

bio-based routes

- **the most important dicarboxylic acid from an industrial point of view**
- **a suitable platform chemical for Biobased production**

—— the International Energy Agency (IEA)

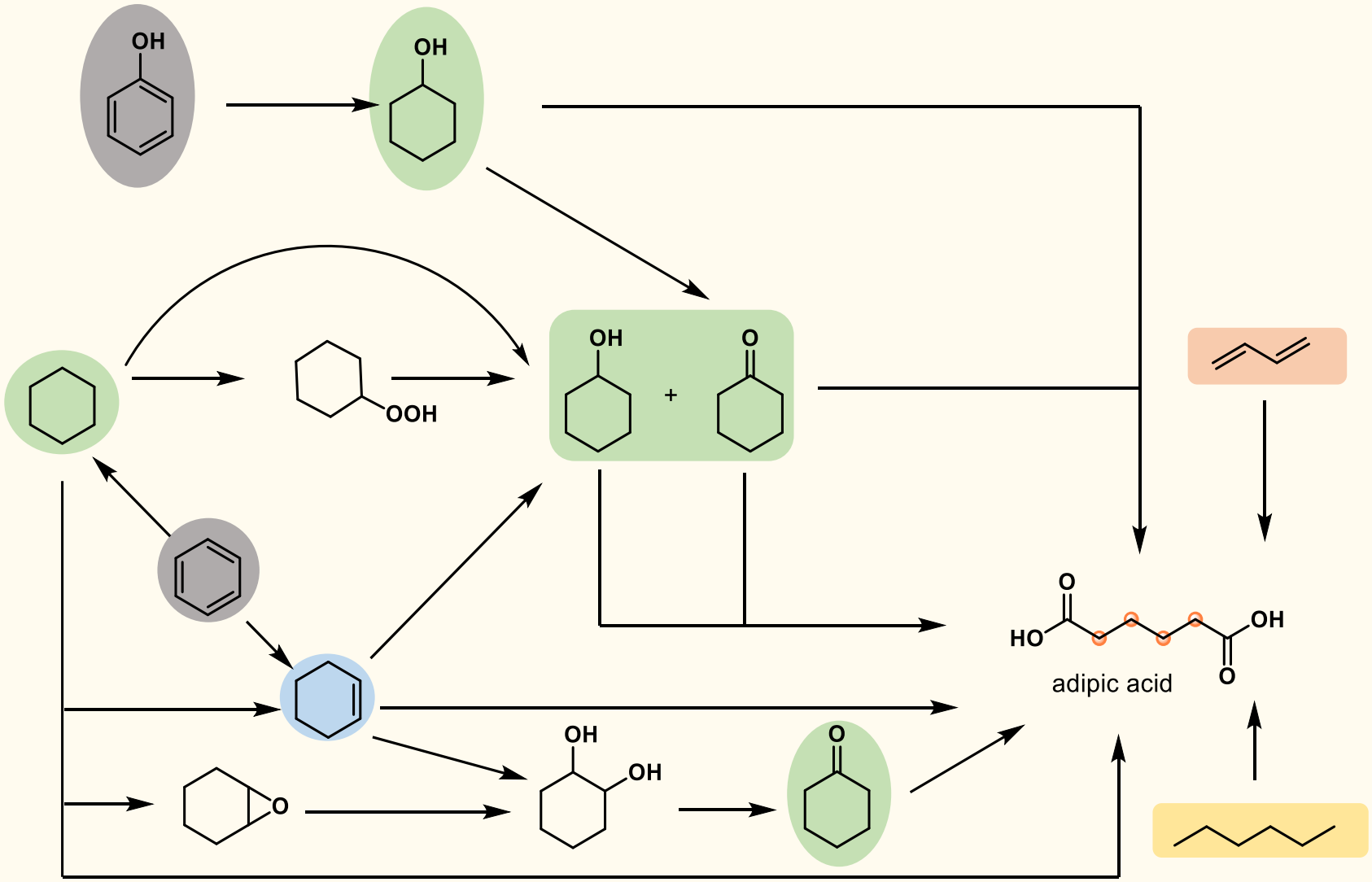


- ✓ **sustainable**
- ✓ **low production costs**
- ✓ **technology-specific market**

acid production	requirements
titer	**50–100 g/L**
rate	**1–3 g/L h^{-1}**
yield	**> 0.5 g/g**

Y. Zhang, *Angew. Chem.* **2014**, *126*, 4284
Y. G. Kim, *Tetrahedron* **2017**, *73*, 4758
B. Xu, *ACS Catal.* **2017**, *7*, 6619
Y. Wang, *Chem. Commun*., **2019**, *55*, 11017
Y. Wang, *Chem. Commun*., **2019**, *55*, 8013
B. Xu, *ACS Appl. Energy Mater*. **2020**, *3*, 99

petrochemical-based routes

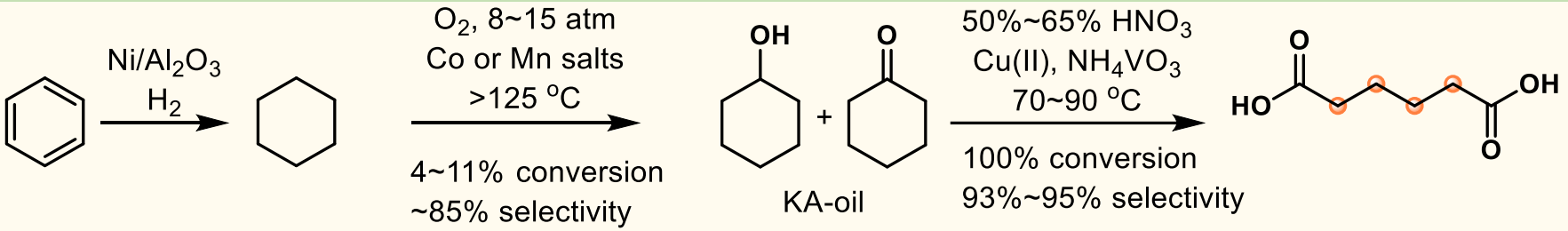


J. C. J. Bart, *Catal. Today* **1991**, *9*, 237
Applied Catalysis A: General **2001**, *211*,1

petrochemical-based routes: Industrial processes

From cyclohexane via cyclohexanone and cyclohexanol (KA oil)

—— the conventional process (by DuPont)

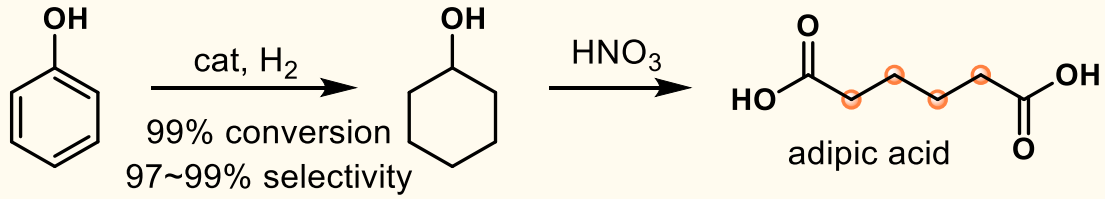


- ✓ mature
- ✓ economical efficiency

- environmental pollution
- large investment
- serious equipment corrosion
- safety concerns

From phenol via cyclohexanol

—— by Solutia and Radici



- ✓ safer and less complex
- ✓ product is extremely pure
- environmental pollution
- large investment
- serious equipment corrosion
- safety concerns

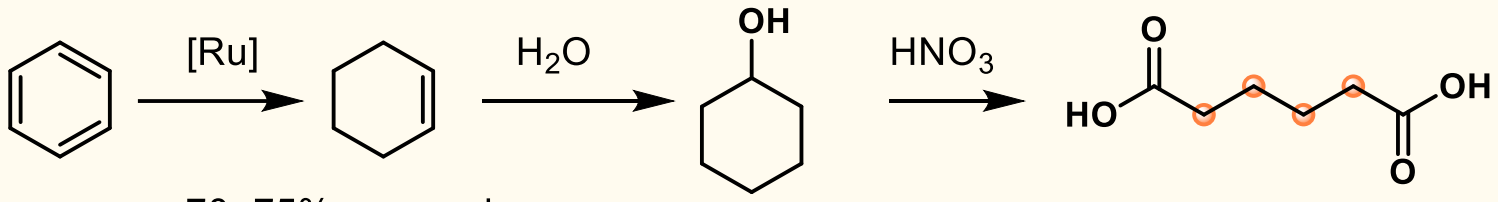
US Patent 4263453, **1981**
Japanese Patents 59184138, **1984**
R. J. Cicerone, *Nature* **1986**, *319*, 109

H. Nagahara and M. Konishi, *ibid*. **1987**, *62*, 45541
W. C. Trogler, *Science* **1991**, *251*, 932
P. E. Tomlinson, *Environ. Prog*. **1994**, *13*, 134

US Patent 5547905, **1996**
A. Scott, *Chem. Week* **1998**, *160*, 37
US Patent 6147256, **2000**

petrochemical-based routes: Industrial processes

From benzene via cyclohexanol by partial hydrogenation and hydration —— (by the Asahi Chemical)



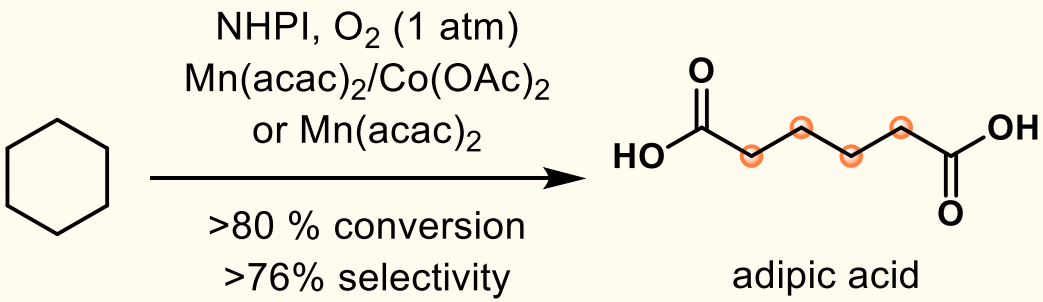
70~75% conversion
80% selectivity

99% selectivity

- ✓ mature and economical efficiency
- ✓ high selectivity

- environmental pollution
- large investment
- serious equipment corrosion
- safety concerns

From cyclohexane use of NHPI as the catalyst —— the new process (by Daicel Chemical)



adipic acid

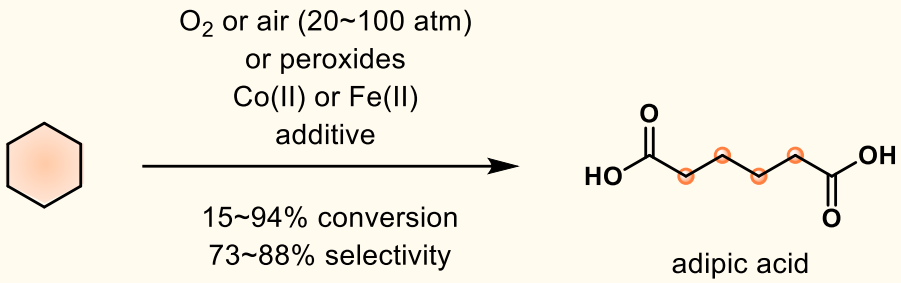
- ✓ one step oxidation
- ✓ environmental friendly
- the high amount of NHPI and decay to phthalimide
- complex

US Patent 4263453, **1981**
Japanese Patents 59184138, **1984**
R. J. Cicerone, *Nature* **1986**, *319*, 109

H. Nagahara and M. Konishi, *ibid*. **1987**, *62*, 45541
W. C. Trogler, *Science* **1991**, *251*, 932
P. E. Tomlinson, *Environ. Prog*. **1994**, *13*, 134

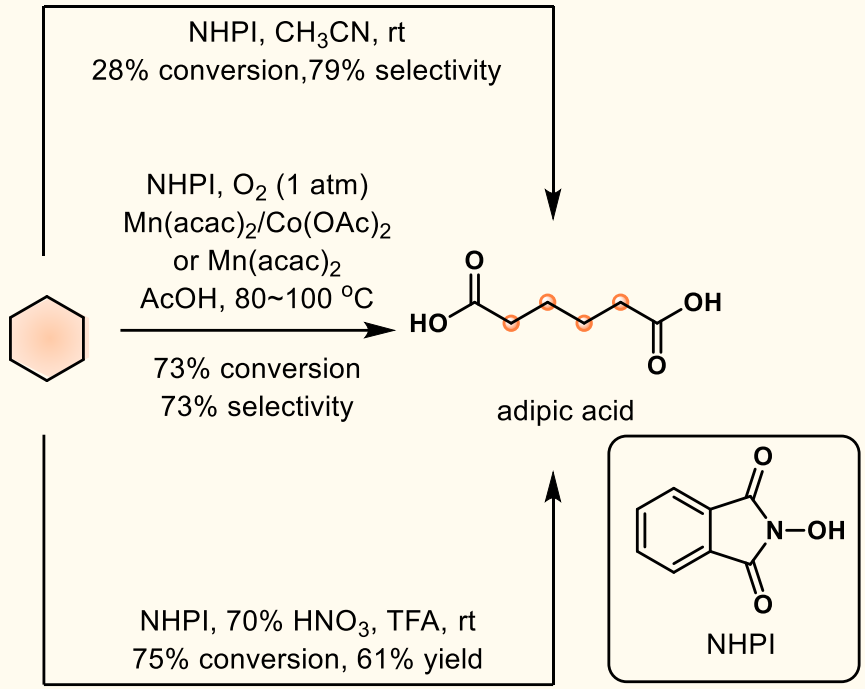
US Patent 5547905, **1996**
A. Scott, *Chem. Week* **1998**, *160*, 37
US Patent 6147256, **2000**

Adipic acid from cyclohexane in Lab



K. Tanaka, *CHEMTECH* **1974**, *6*, 555
J. G. D. Schulz, *J. Org. Chem*. **1973**, *38*, 3729
US Patent 4263453, **1981**
US Patent 4902827, **1990**
J.Singh, *J. Chem. Tech. Biotechnol*. **1991**, *50*, 57
BASF, WO 9,407,833, **1994**
US Patent 5547905, **1996**
J. M. Thomas, *Catalysis Letters* **1998**, *55*, 15
J. M. Thomas, *Angew. Chem. Int.* **2000**, *39*, 2310
J. M. Thomas, *Angew. Chem. Int*. **2000**, *39*, 2313
US Patent 6147256, **2000**
Y. Ishii *J. Org. Chem*. **2001**, *66*, 7889

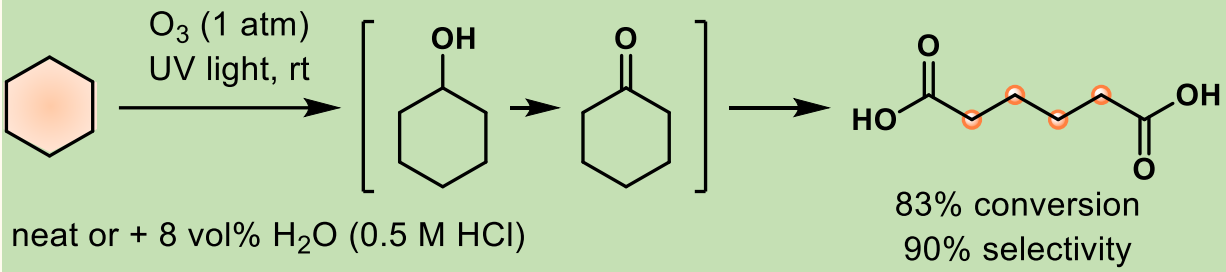
- ✓ **one step oxidation**
- ✓ **environmental friendly**
- • **low conversion**
- • **low selectivity**
- • **additives**
- • **tough conditions**



Y. Ishii, *Org, Proc. Res. & Dev*. **1998**, 2, 255
O. Onomura, *Org. Process Res. Dev.* 2018, *22*, 1312
W. Zhong and L. Mao, *Journal of Catalysis* 2019, *378*, 256

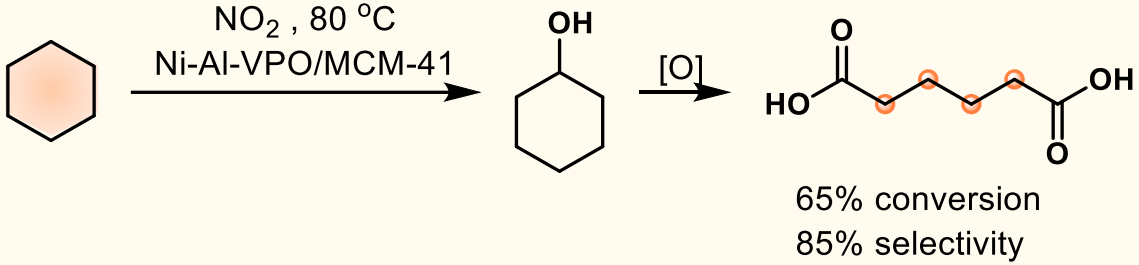
- ✓ **one step oxidation**
- ✓ **environmental friendly**
- • **the high amount of NHPI and decay to phthalimide**
- • **complex**

Adipic acid from cyclohexane in Lab



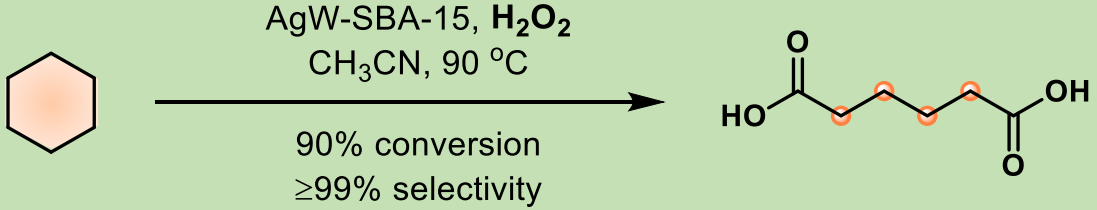
- ✓ one step oxidation
- ✓ environmental friendly
- ✓ more economical
- • explosive organic peroxides
- • technical issues

K. C. Hwang, *Science* **2014**, *346*, 1495



- ✓ mild condition
- ✓ NO_2 as oxidant, green
- • scaled-up issue
- • materials recovery issue
- • low conversion
- • low selectivity

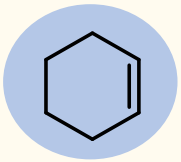
H. Luo, *Ind. Eng. Chem. Res*. **2016**, *55*, 3729



- ✓ one step oxidation
- ✓ high conversion
- ✓ high selectivity
- ✓ green
- • scaled-up issue
- • materials recovery issue

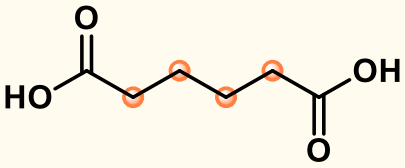
A. Bordoloi, ACS Appl. Nano Mater. **2019**, 2, 5989

Adipic acid from cyclohexene in Lab



30% H_2O_2, Na_2WO_4
$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$

90%



adipic acid

- ✓ one step oxidation
- ✓ less corrosive
- ✓ clean, safe, and reproducible
- • expensive systems
- • PTC- environmental pollution

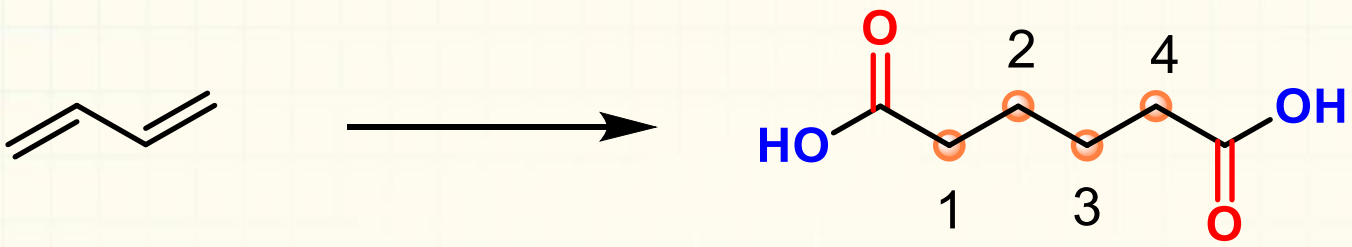
R. Noyori, *Science* **1998**, *281*,1646

Condition	Yield	References
➢ $[PO_4\{W_2O_2(m\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ ➢ Na_2WO_4 with H_2SO_4 ➢ microflow packed-bed reactors ➢ Pickering Interfacial Catalysist systems ➢ Microemulsions ➢ Inert Polymeric Membrane Reactor ➢ microwave irradiation ➢ ……	59%-95%	J. Chen, *Green Chem.* **1999**, *1*, 275 E. Perez, *Tetrahedron* **2010**, *66*, 7124 E. Drioli, *OPR&D* **2010**, *14*, 252 K. Holmberg, *Green Chem*. **2010**, *12*, 1861 X. Wang, *Catalysis Today* **2011**, *175*, 619 M. Tang, *J. Mol. Struct*., **2011**, *992*, 1 C. O. Kappe, *ChemSusChem* **2013**, *6*, 978 V. Hessel, *Ind. Eng. Chem. Res*. **2016**, *55*, 2669 V. N. Rataj, *Chem. Sci*., **2019**, *10*, 501 ……

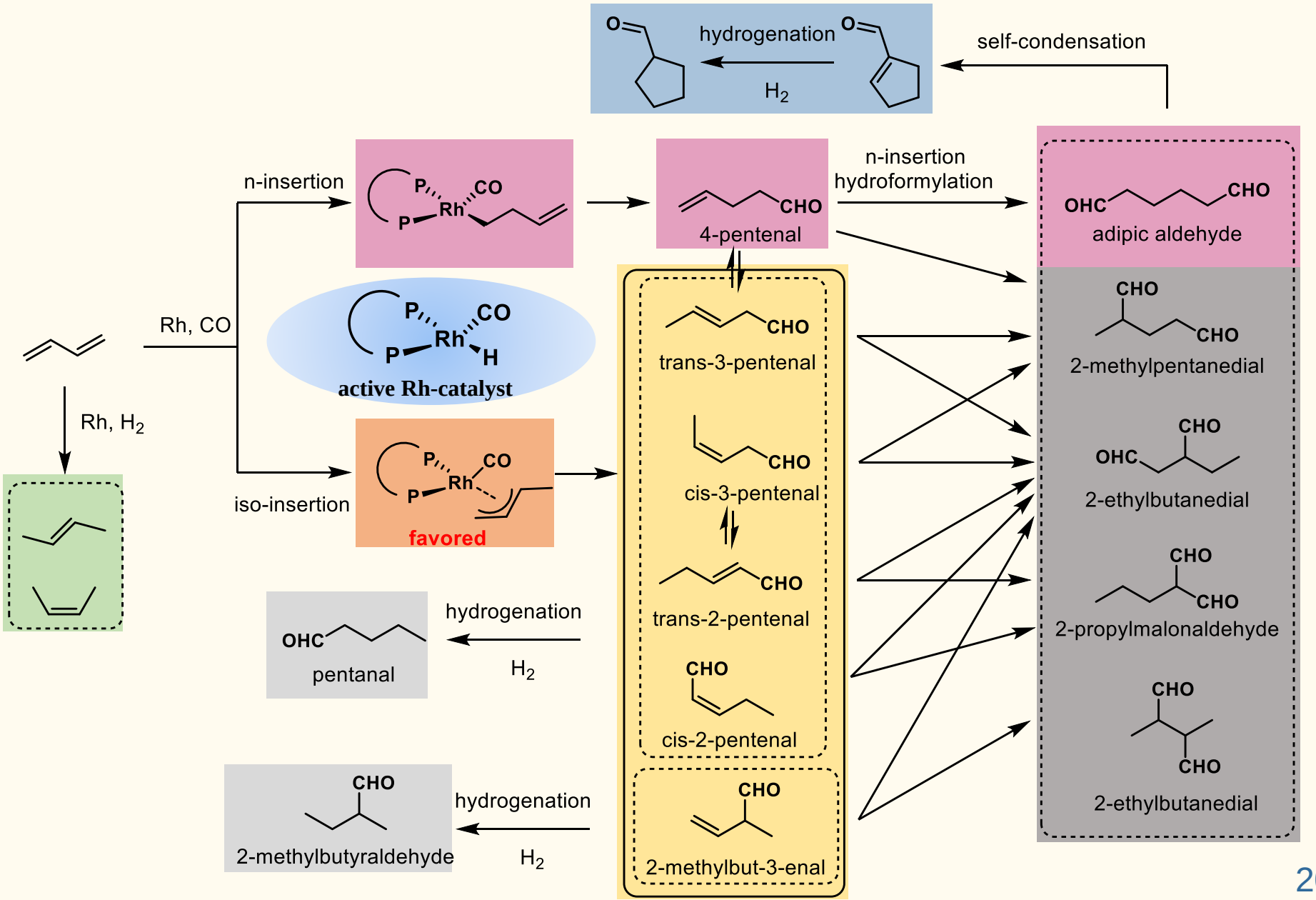
Advantages and disadvantages (high conversion and selectivity routes)

METHODS		ADVANTAGES	DISADVANTAGES
Bio-based		sustainable specific market low production costs	titer rate yield scaled-up issues
	KA oil, HNO_3	economical efficiency mature technology	environmental pollution large investment equipment corrosion safety concerns
	ozone and UV light	one-step oxidation Green economical efficiency	safety concerns technical issues
	H_2O_2, Ag/WO_3 material	one-step oxidation Green	scaled-up materials recovery
	NHPI / $Mn(acac)_2$	one-step oxidation green	high amount of NHPI NHPI decay to phthalimide
	via cyclohexanol, HNO_3	safer less complex low investment costs	environmental pollution large investment serious equipment corrosion safety concerns
	H_2O_2, PTC, cat (Na_2WO_4)	one-step oxidation clean, safe, and reproducible less corrosive no operational problems	>4 eq H_2O_2, cost prohibitive PTC is expensive environmental pollution

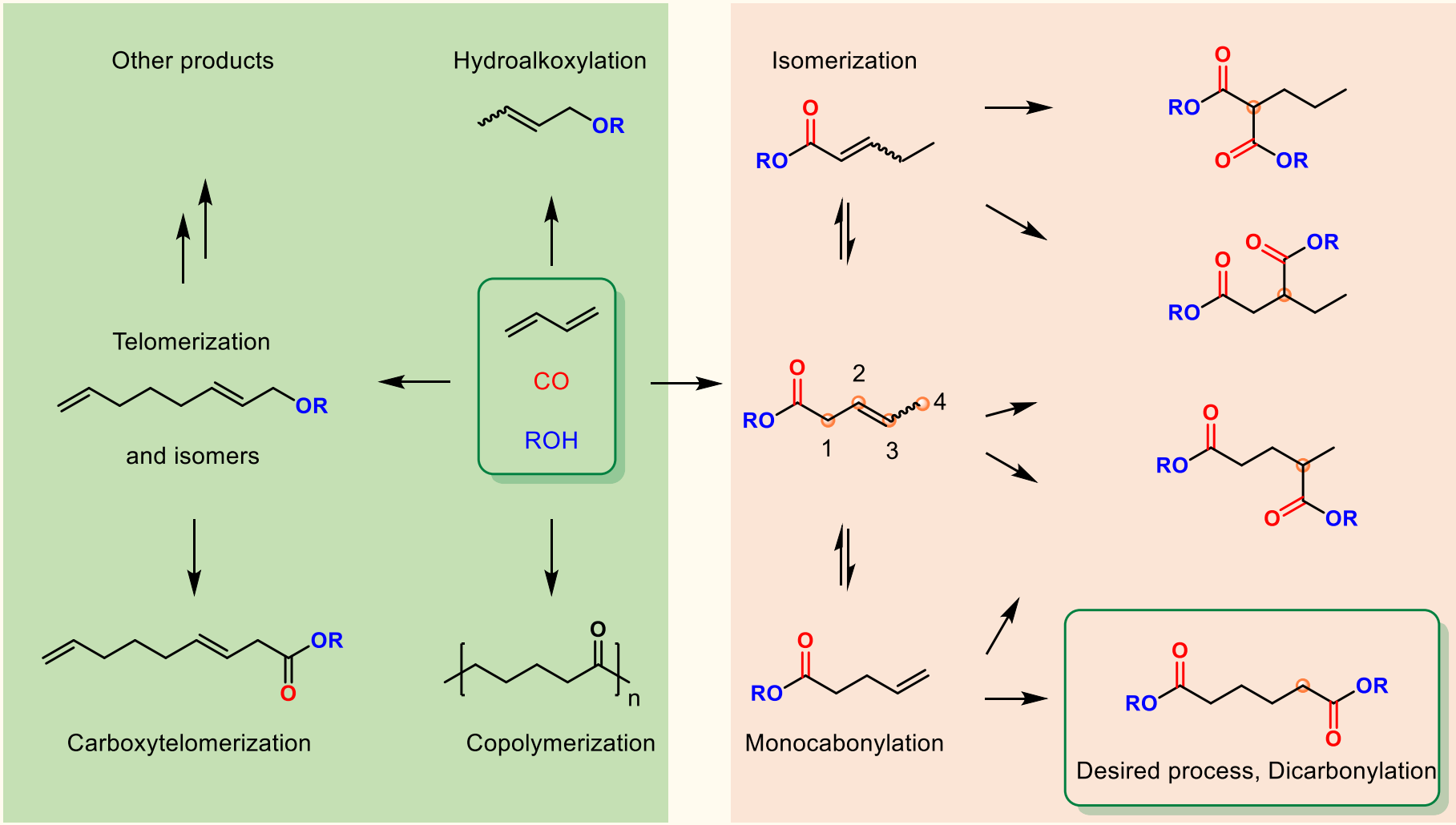
Contents



Dihydroformylation of 1,3-butadiene



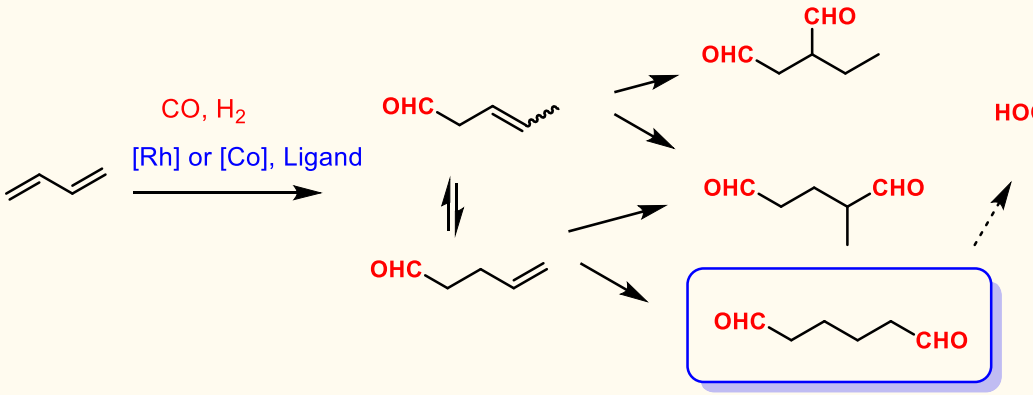
Reaction network involved in synthesis of adipates from 1,3-butadienes



P. Hofmann, *Organometallics* **2011**, *30*, 3643
P. Hofmann, *Organometallics* **2015**, *34*, 841
B. Subramaniama, *Molecular Catalysis* **2020**, *484*, 110721
W. W. Jager, Patent WO 2000056695, **2000**
K. Nikolaus, Patent DE 2037782, **1970**

Adipic acid from 1,3-butadiene

Sequential hydroformylation —— the more traditional approach

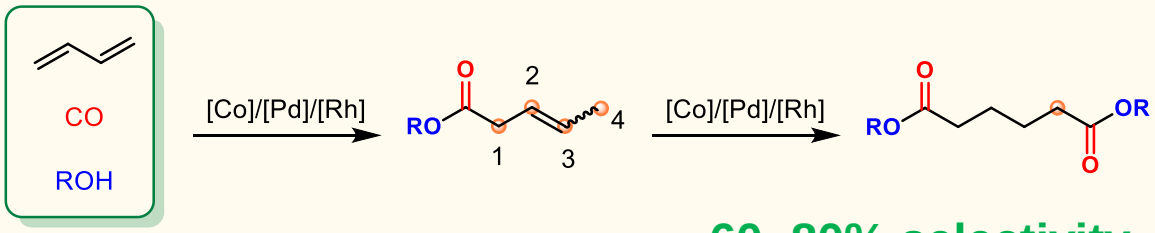


- slow reaction rate
- low regioselectivity

MAX~50% selectivity

J.L.R. Williams, *J. Org. Chem*. **1952**, *17*, 980
B. Fell, *Tetrahedron Lett.* **1969**, *10*, 2721
B. Fell, *J. Mol. Catal*. **1980**, *8*, 329
C.F. Roobeek, *J. Mol. Catal*. **1985**, *31*, 345
S. Bertozzi，*Journal of Organometallic Chemistry* **1995**, *487,41*
Y. Ohgomori, *Journal of Molecular Catalysis A: Chemical* **1998**, *133*, 289

Sequential hydroxycarbonylation —— developed by BASF



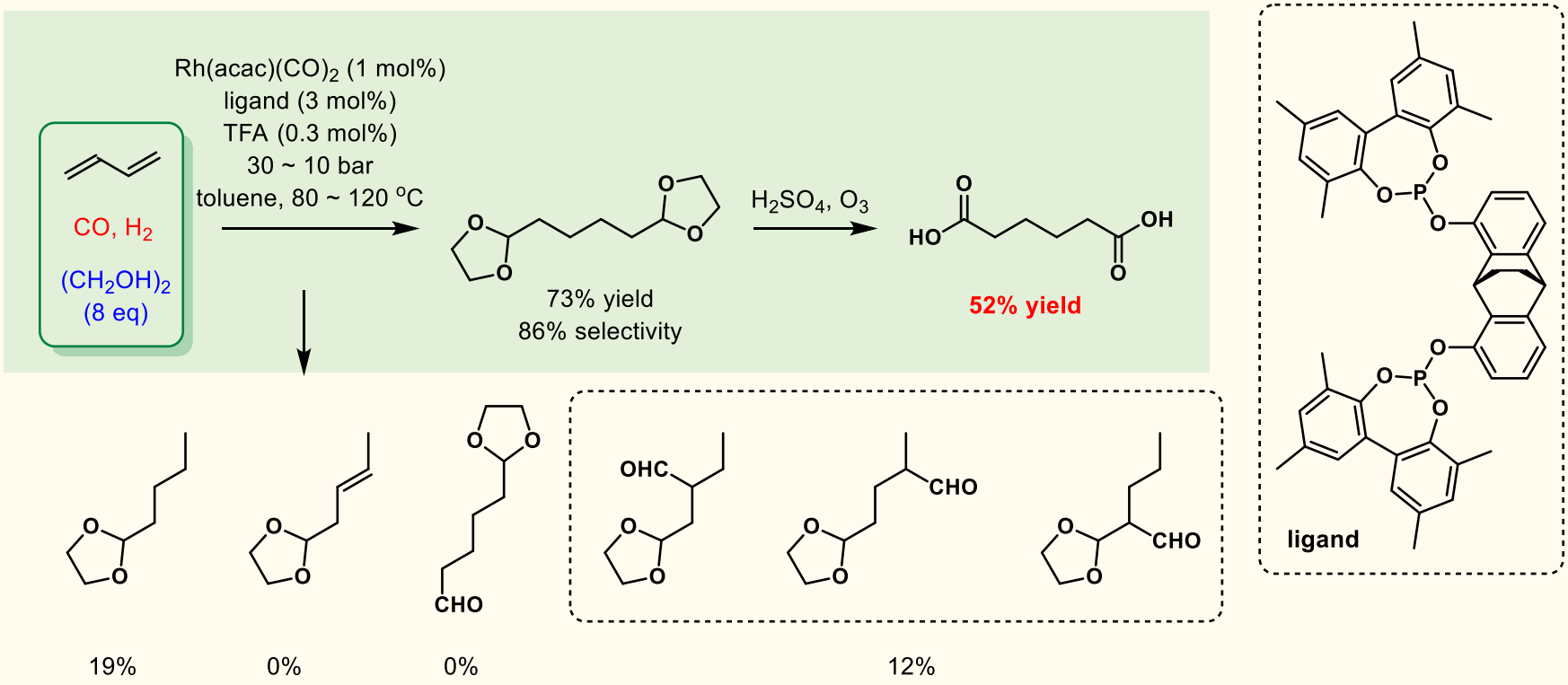
- multistep reactions
- insufficient selectivity
- high temperature
- high pressure
- expensive ligands

60~80% selectivity

M. T. Musser, *in Ullmann's Encyclopedia of Industrial Chemistry* (Wiley, **2005**)
W. Bertleff, M. Roeper, X. Sava, *in Ullmann's Encyclopedia of Industrial Chemistry* (Wiley, **2012**)
M. Beller, *Angew. Chem. Int. Ed*. **2014**, *53*, 9030

Adipic acid from 1,3-butadiene

Double-n-Selective Hydroformylation via acetal-protected dialdehyde



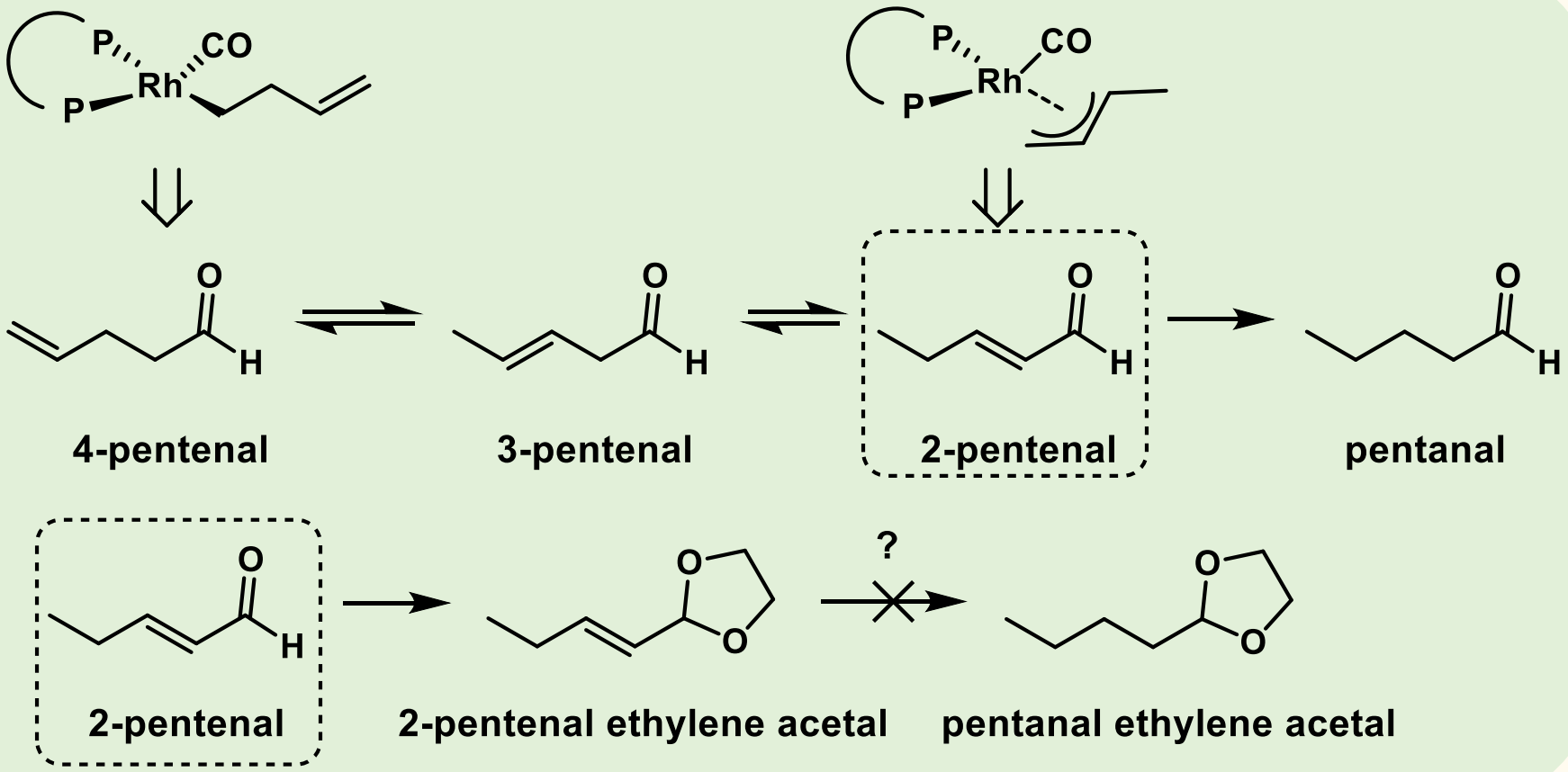
Selectivity = linear diacetal/all diacetal derivatives

- multistep reactions
- insufficient selectivity
- 8 eq glycols

T. Schaub & P. Hofmann, *ACS Catal*. **2016**, *6*, 2802

Adipic acid from 1,3-butadiene

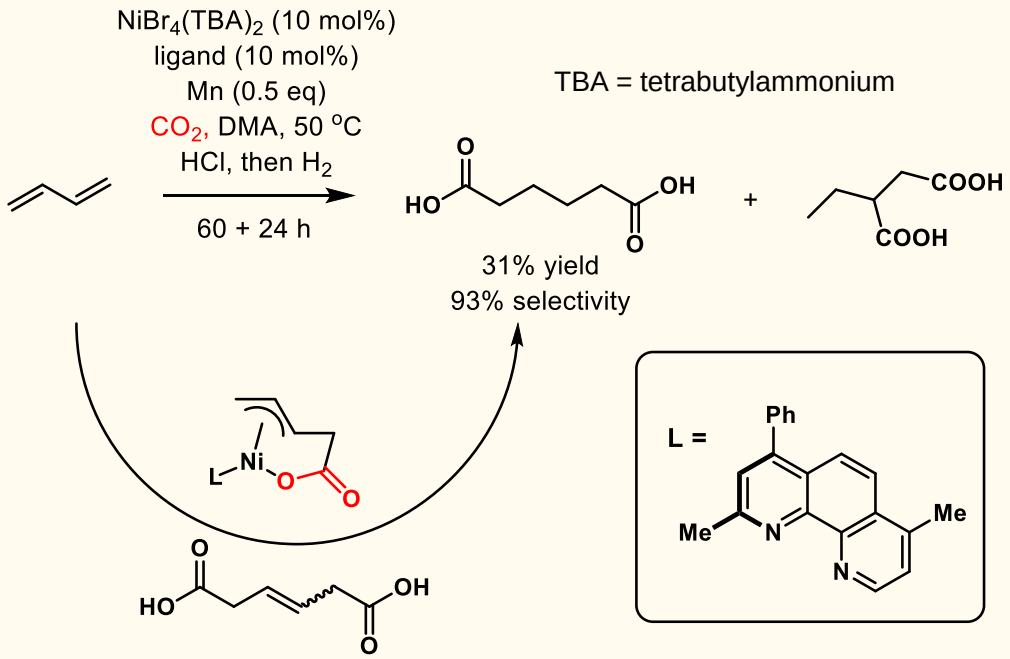
Double-n-Selective Hydroformylation via acetal-protected dialdehyde

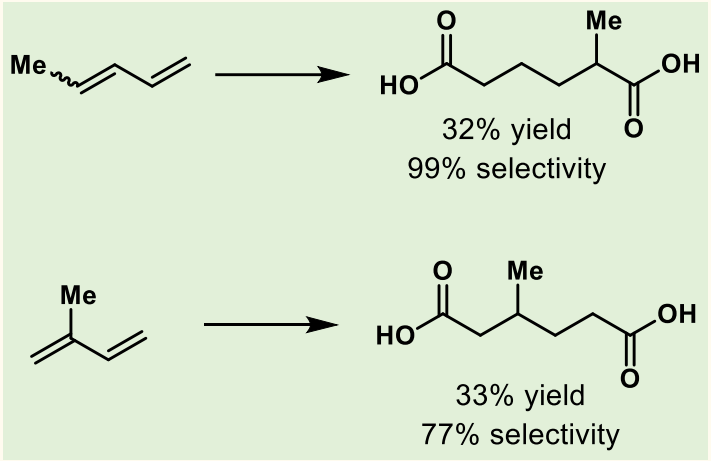


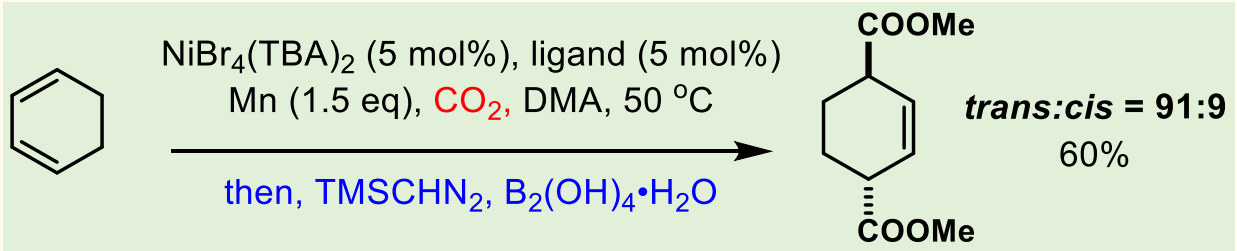
T. Schaub & P. Hofmann, *ACS Catal*. **2016**, *6*, 2802

Adipic acid from 1,3-butadiene

Ni-Catalyzed Site-Selective Dicarboxylation of 1,3-Dienes with CO_2







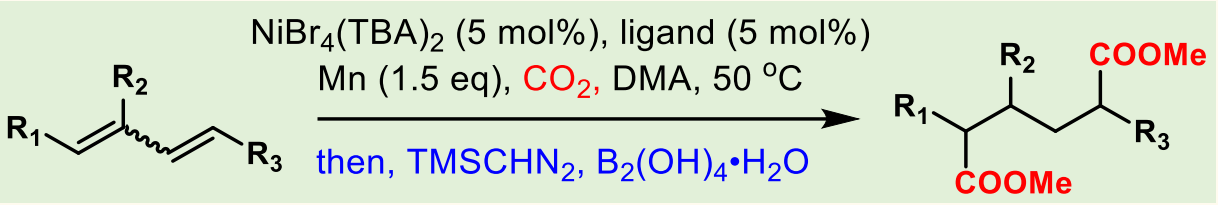
- two step, complex
- low yield
- high catalyst loading
- 0.5 eq Mn
- slow reaction rate
- scale up issue

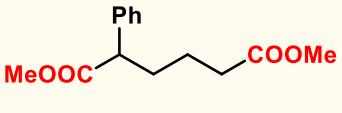
M. Mori, *J. Am. Chem. Soc.* **2001**, *123*, 2895

R. Martin, *J. Am. Chem. Soc.* **2018**, *140*, 2050

Adipic acid from 1,3-butadiene

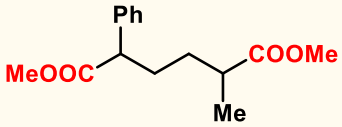
Ni-Catalyzed Site-Selective Dicarboxylation of 1,3-Dienes with CO_2



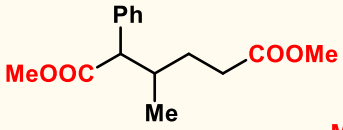


74%

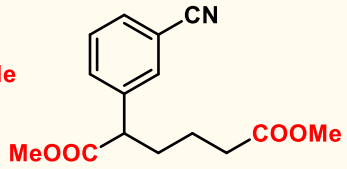
73% (Using *E*-SM)



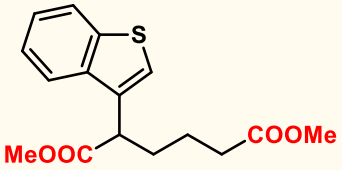
68%, dr = 1:1



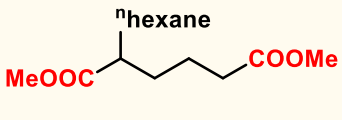
75%, dr = 1.5:1



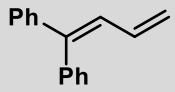
51%



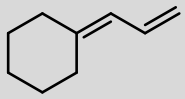
60%



73%



no conversion



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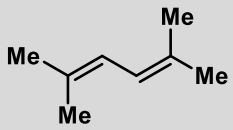
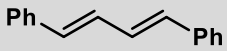


no conversion



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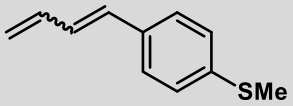

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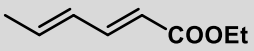
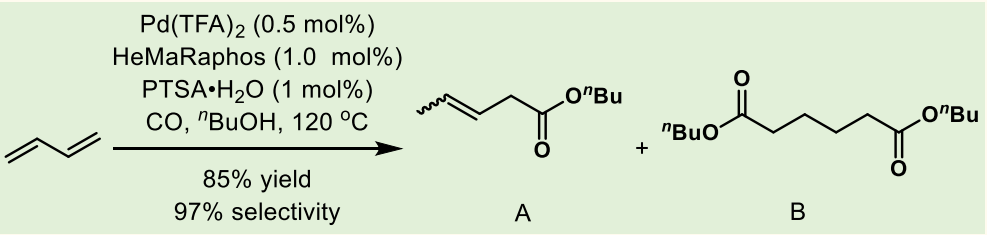


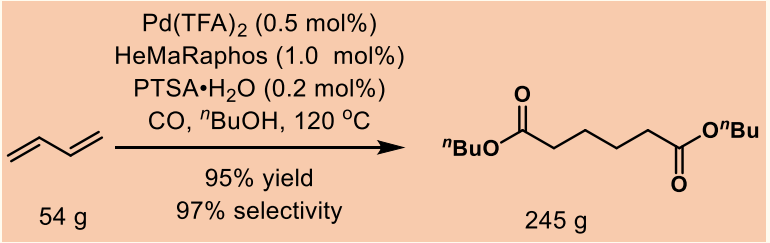
no conversion

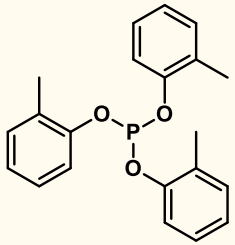
R. Martin, *J. Am. Chem. Soc.* **2018**, *140*, 2050

Adipic acid from 1,3-butadiene

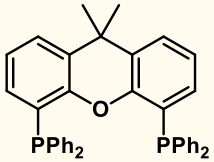
Direct synthesis of adipic acid esters via Pd-catalyzed carbonylation of 1,3-dienes



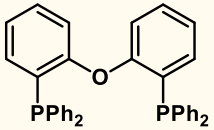




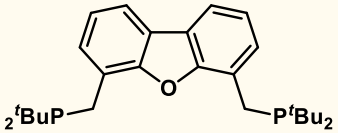
42% A, 0% B
0% selectivity



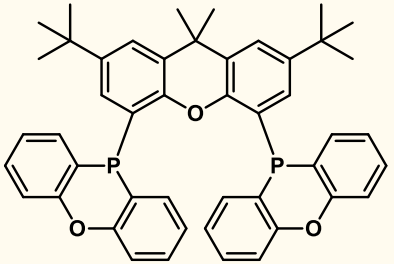
49% A, 25% B
79% selectivity



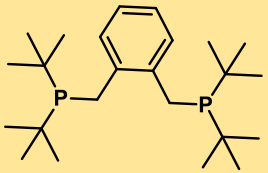
15% A, 0% B
0% selectivity



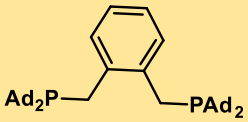
72% A, 4% B
80% selectivity



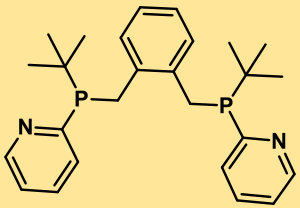
0% A, 16% B
79% selectivity



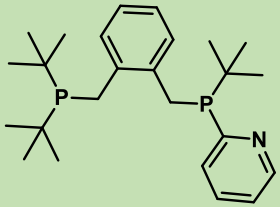
60% A, 18% B
97% selectivity



63% A, 13% B
95% selectivity



7% A, 77% B
48% selectivity



7% A, 85% B
97% selectivity

HeMaRaphos:
7 steps, < 20% yield

Selectivity represents the ratio of linear diester to all diesters.

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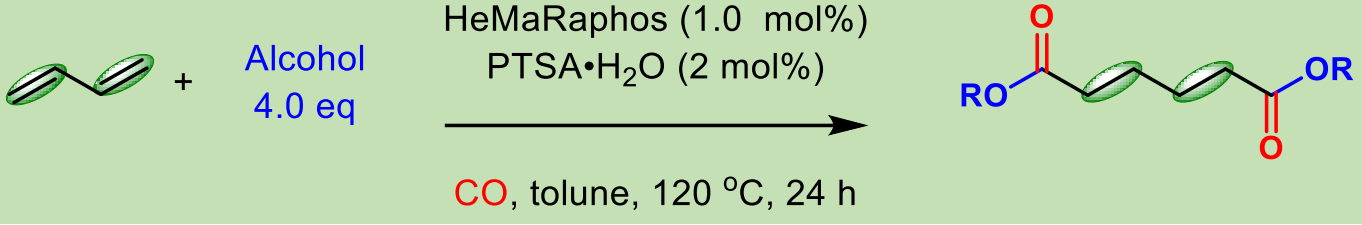
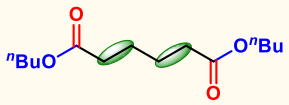
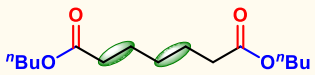
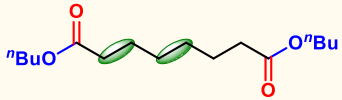
Palladium-catalyzed dicarbonylation of 1,2-dienes

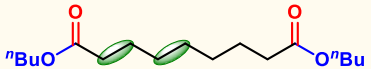
Direct synthesis of adipic acid esters via Pd-catalyzed carbonylation of 1,3-dienes

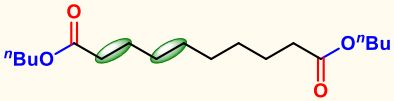


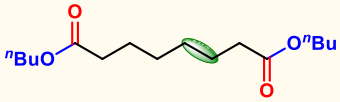

85%, (97/3)

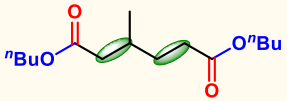

84%, (95/5)

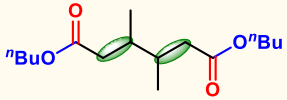

82%, (95/5)

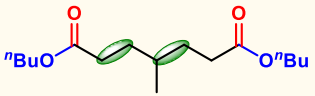

79%, (92/8)

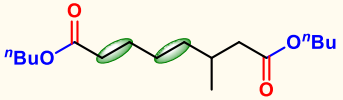

74%, (90/10)

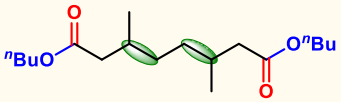

81%, (92/8)

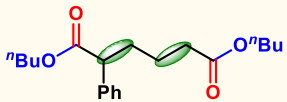

78%, (98/2)


53%, (97/3)

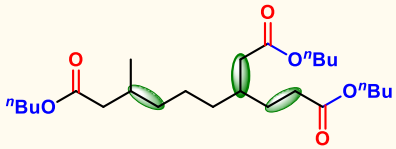

77%, (91/9)

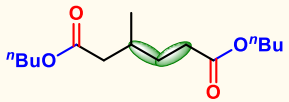

73%, (94/6)

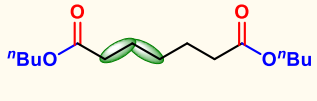

37%, (95/5)



82%, (91/9)


61%, (91/9)


81%, (98/2)


84%, (93/7)

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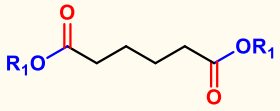
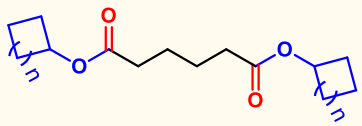
Palladium-catalyzed dicarbonylation of 1,3-dienes

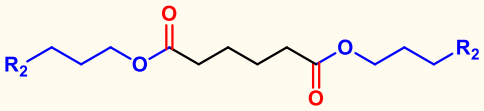
Direct synthesis of adipic acid esters via Pd-catalyzed carbonylation of 1,3-dienes



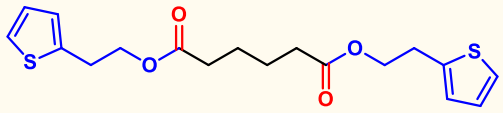
R_1 = Me, 81% (97/3)
R_1 = Et, 82% (97/3)
R_1 = ^{n}Pr, 88% (97/3)
R_1 = $^n C_5H_{11}$, 92% (97/3)
R_1 = $^n C_6H_{13}$, 83% (96/4)
R_1 = $^n C_7H_{15}$, 86% (97/3)
R_1 = $^n C_8H_{17}$, 87% (96/4)
R_1 = ^{i}Pr, 83% (98/2)
R_1 = 2-Bu, 82% (97/3)
R_1 = 2-C_5H_{11}, 85% (97/3)
R_1 = 3-C_5H_{11}, 71% (97/3)
R_1 = 2-C_6H_{13}, 76% (97/3)
R_1 = 2-C_6H_{13}, 77% (96/4)



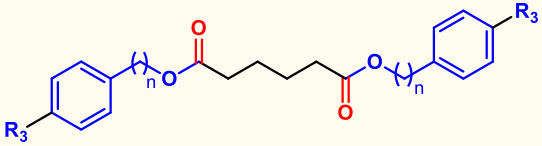
n = 1, 87% (97/3)
n = 2, 82% (98/2)
n = 3, 83% (96/4)
n = 4, 78% (96/4)
n = 5, 73% (95/5)



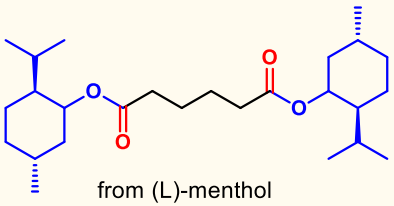
R_2 = F, 86% (95/5)
R_2 = CF_3, 82% (92/8)
R_2 = Cl, 85% (95/5)
R_2 = OCH_3, 78% (97/3)



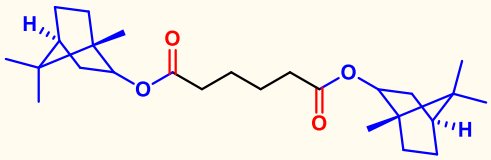
71% (94/6)



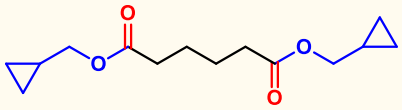
n = 1, R_3 = H, 88% (98/2)
n = 1, R_3 = Cl, 75% (93/7)
n = 3, R_3 = H, 74% (96/4)
n = 4, R_3 = H, 75% (97/3)



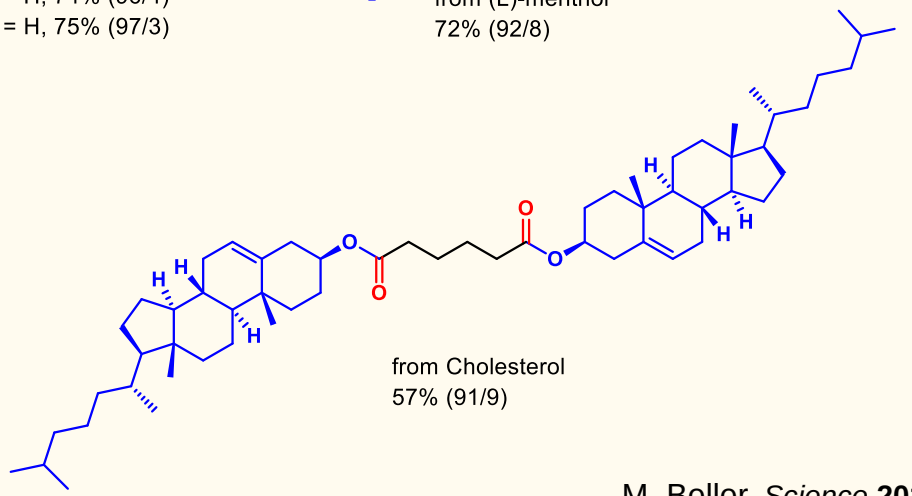
from (L)-menthol
72% (92/8)



from (L)-borneol
71% (94/6)



83% (94/6)



from Cholesterol
57% (91/9)

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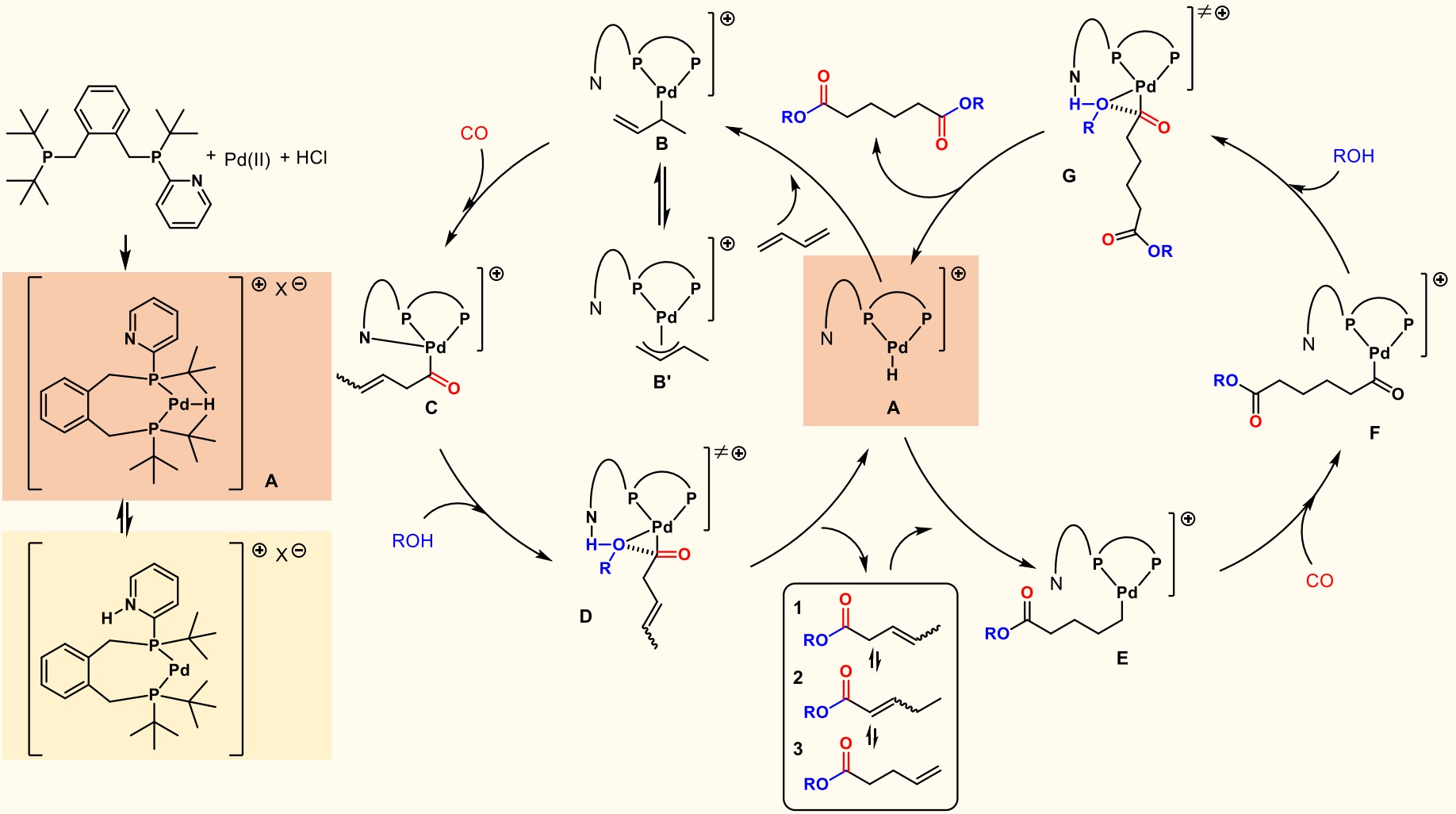
Catalytic mechanism

Direct synthesis of adipic acid esters via Pd-catalyzed carbonylation of 1,3-dienes



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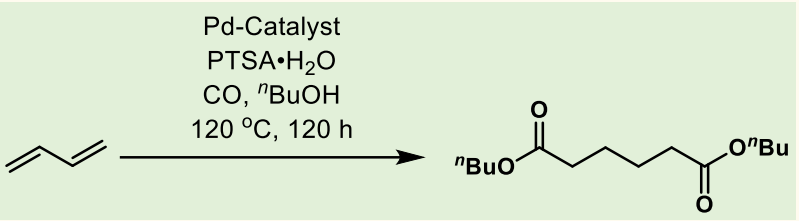
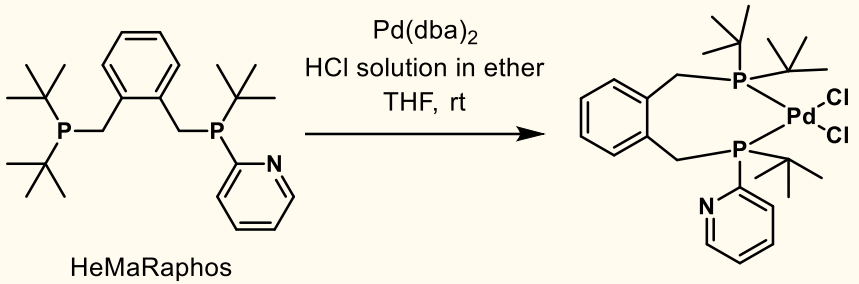
TON experiments

Direct synthesis of adipic acid esters via Pd-catalyzed carbonylation of 1,3-dienes





HeMaRaphos

Entry	Catalyst loading	Yield (%)	Selectivity	TON
1	10^{-4}	27	93/7	2700
2	10^{-3}	86	89/11	860
3	10^{-4}	86	91/9	8600
4	**10^{-5}**	**64**	**92/8**	**64000**

the ratio of products and yield were determined by GC analysis with mesitylene as the internal standard. The products selectivity is the ratio of linear diesters to branched diesters. TON = turnover number = reacted butadiene (mmol) /mmol Pd.

reaction conditions

1. butadiene (2.0 mmol, solution in toluene), ^{n}BuOH (3.0 mL), **$PdCl_2$** (0.0002 mmol, accurately weigh 2mg $PdCl_2$, dissolved in 56.5mL ^{n}BuOH, stir well, then take 1mL of this solution add to the reaction system), HeMaRaphos (8.3 mg, 0.02 mmol), PTSA·H_2O (7.7 mg, 0.04 mmol), CO (40 atm), 120 ^{o}C, 120 h;

2.3.4. butadiene (10.0 mmol, gas), ^{n}BuOH (20.0 mL), **$PdCl_2$-HeMaRaphos** complex (accurately weigh 2mg $PdCl_2$-HeMaRaphos complex, dissolved in 33.7 mL ^{n}BuOH, stir well, then measure different volumes for different reactions, for example for entry 3, take 10 mL of this solution to the reaction system), PTSA·H_2O (38 mg, 0.2 mmol), CO (40 atm), 120 ^{o}C, 120 h

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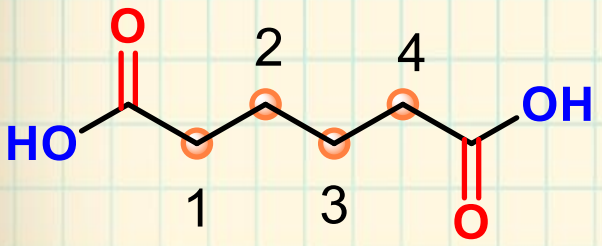
c&en NEWS: Evonik touts a carbonylation advance

c&en NEWS: Evonik touts a carbonylation advance

In partnership with the Leibniz Institute for Catalysis, Evonik Industries has developed what is says is the first direct carbonylation of 1,3-butadiene. The partners succeeded in double carbonylating the common olefin to produce adipic acid salts, including one used to make nylon 6. At the heart of the process is a novel palladium catalyst based on a phosphine ligand.

——(2020/01/13 by Alex Scott)

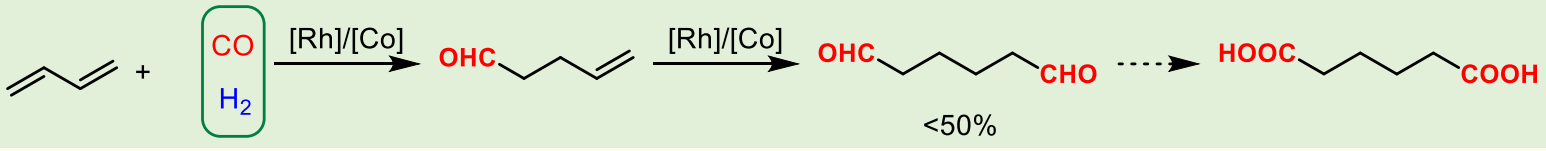
Contents

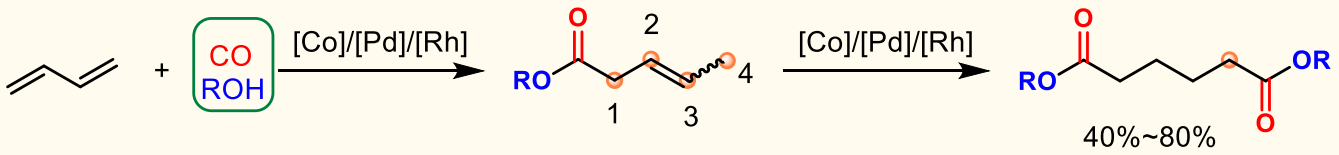


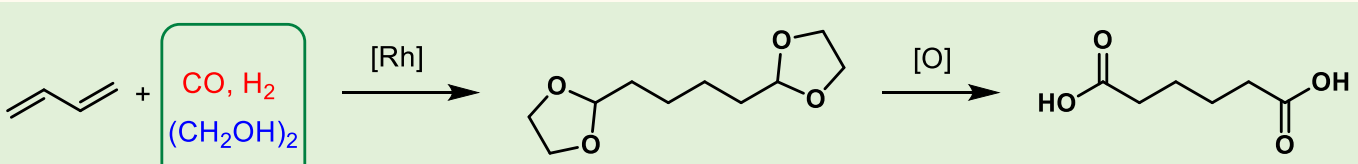
Advantages and disadvantages (high conversion and selectivity routes)

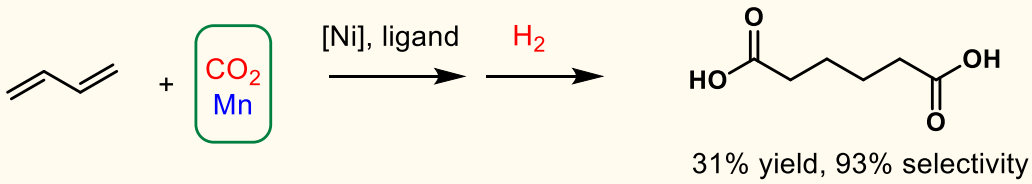
METHODS		ADVANTAGES	DISADVANTAGES
Bio-based		sustainable specific market low production costs	titer rate yield scaled-up issues
	KA oil, HNO_3	economical efficiency mature technology	environmental pollution large investment equipment corrosion safety concerns
	ozone and UV light	one-step oxidation Green economical efficiency	safety concerns technical issues
	H_2O_2, Ag/WO_3 material	one-step oxidation Green	scaled-up materials recovery
	NHPI / $Mn(acac)_2$	one-step oxidation green	high amount of NHPI NHPI decay to phthalimide
	via cyclohexanol, HNO_3	safer less complex low investment costs	environmental pollution large investment serious equipment corrosion safety concerns
	H_2O_2, PTC, cat (Na_2WO_4)	one-step oxidation clean, safe, and reproducible less corrosive no operational problems	>4 eq H_2O_2, cost prohibitive PTC is expensive environmental pollution

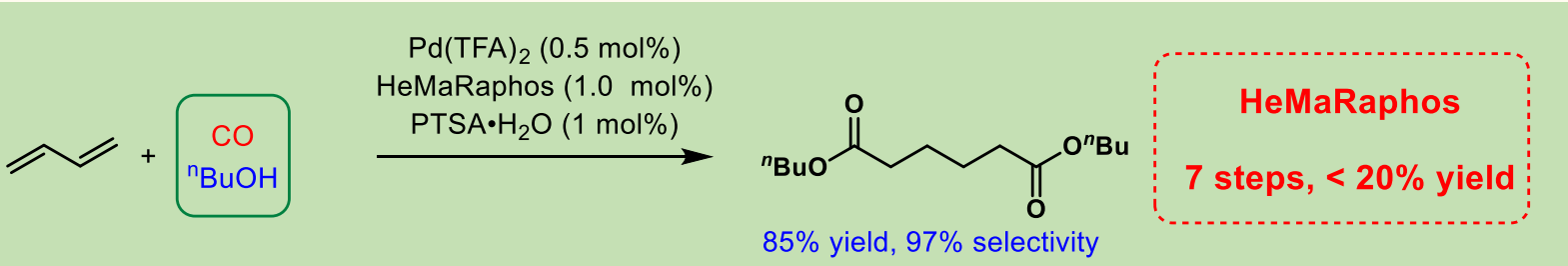
Conclusion: carbonylation of 1,3- butadiene



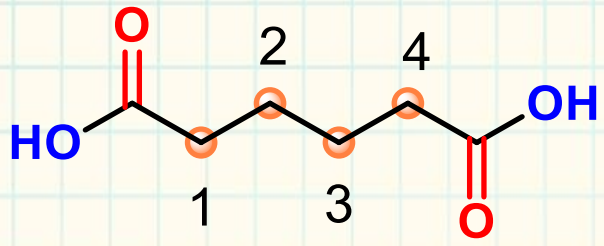


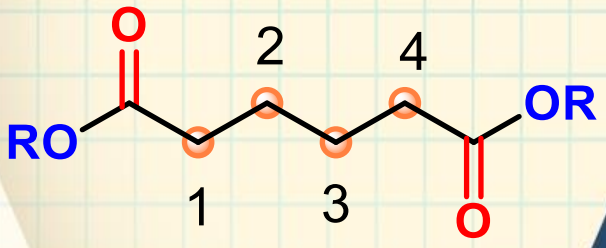




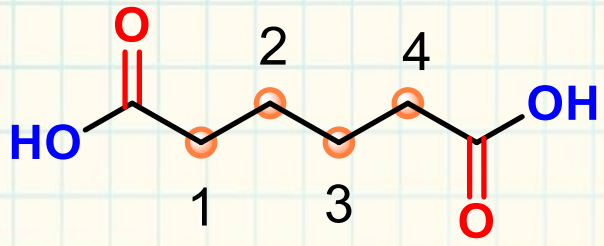


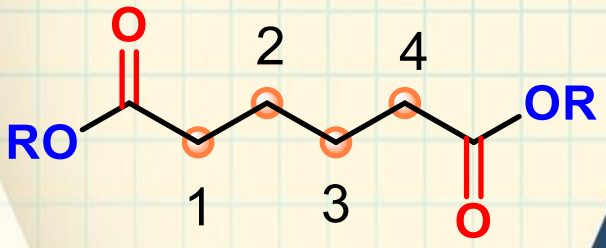
★commercial reactants ★no by-products ★low consumables
★ low operating costs ★no N_2O emission ★ acceptable energy requirements





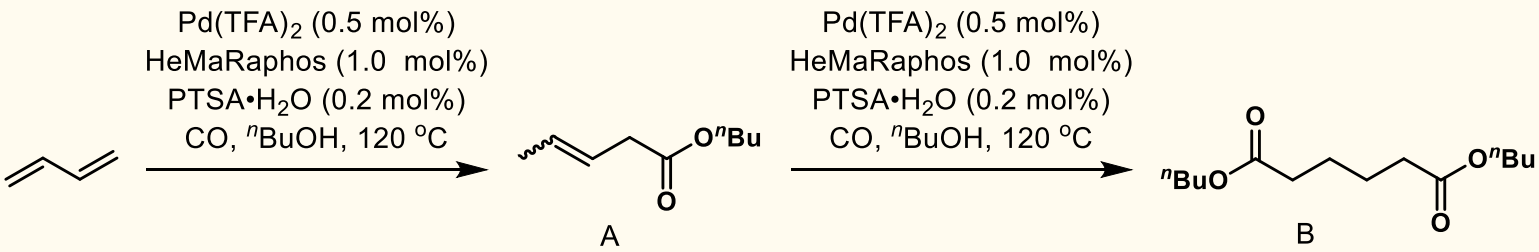
Thanks For Your Attention!

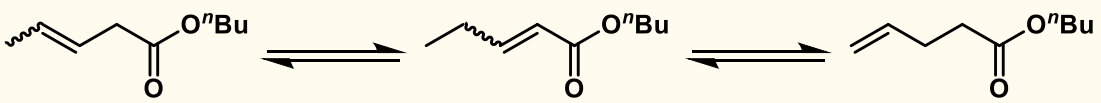


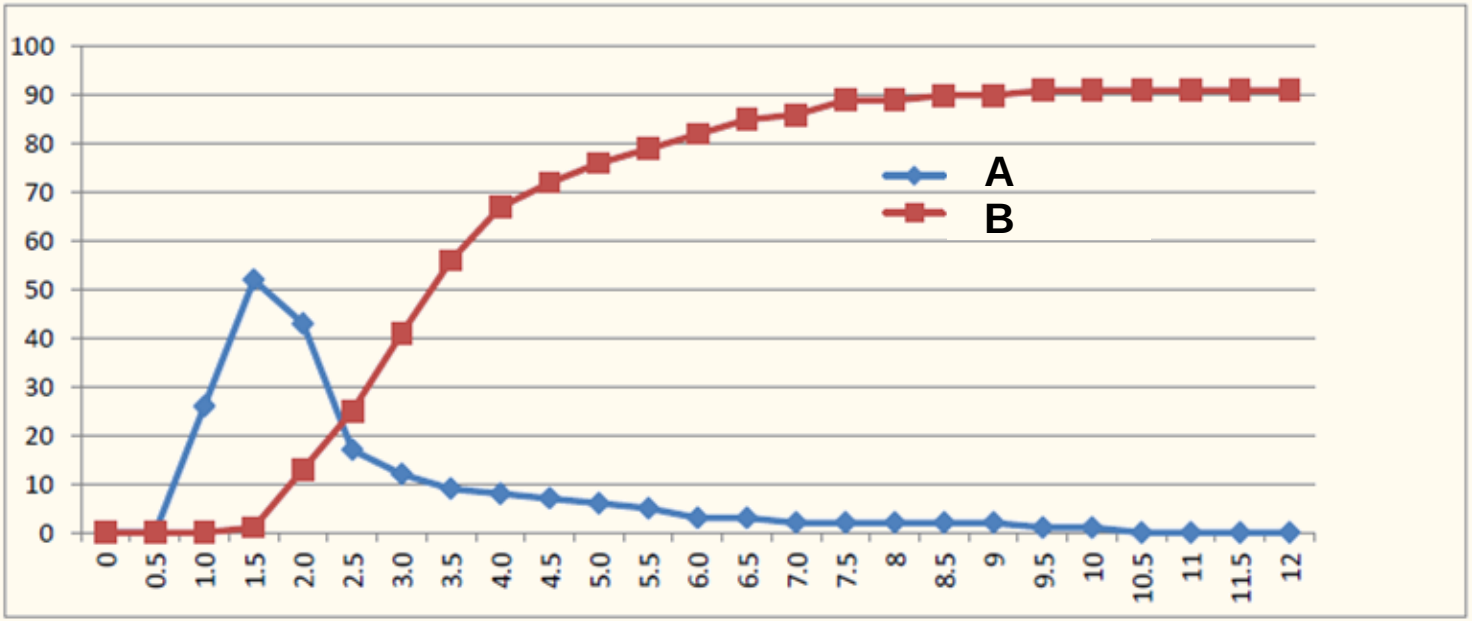


Thanks For Your Attention!

Kinetic monitoring experiment







The *X*-axis represents the reaction time and the *Y*-axis represents the reaction yield. Reaction conditions: butadiene (20 mmol), $Pd(TFA)_2$ (0.005 mmol, 0.5 mol%), ligand (0.01 mmol, 1.0 mol%), $PTSA{\cdot}H_2O$ (2 mol%), ^{n}BuOH (25 mL), CO (40 atm), 120 °C; the GC yield were determined by GC analysis with mesitylene as the internal standard.

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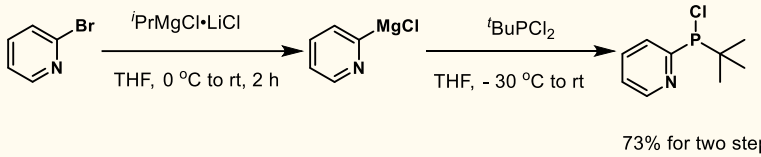
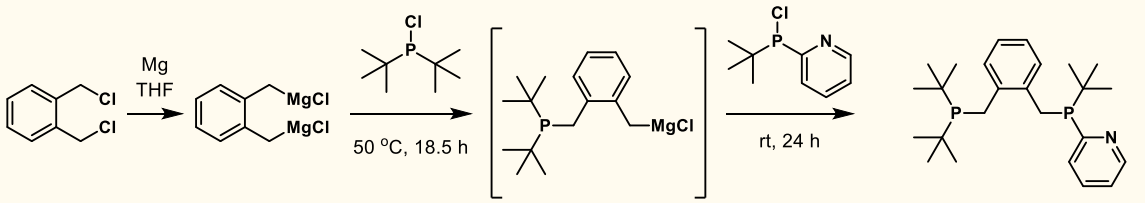
Synthetic route of HeMaRaphos

The new ligand HeMaRaphos was synthesized according to following procedure:

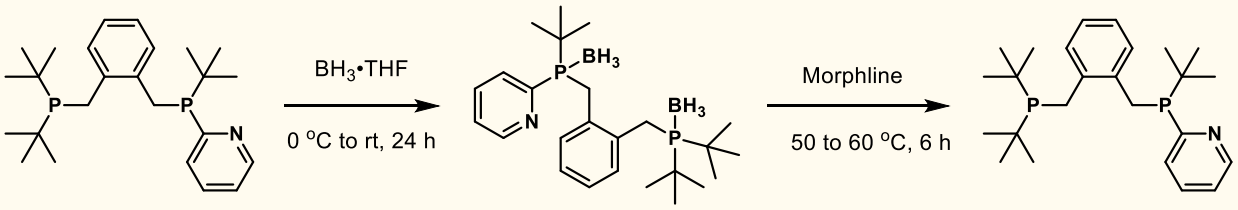


73% for two steps

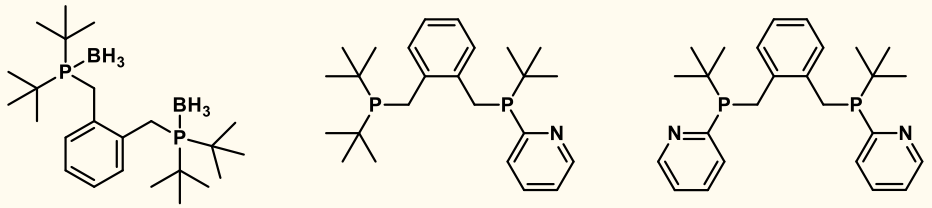


23%, light yellow solid.

A mixture of several phosphines is obtained, followed by separation and purification:



mixture | 25% | 23%



18% | 25% | 8%

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