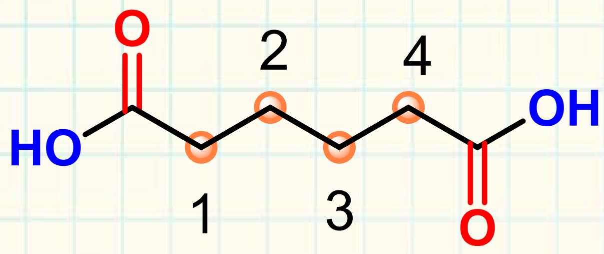
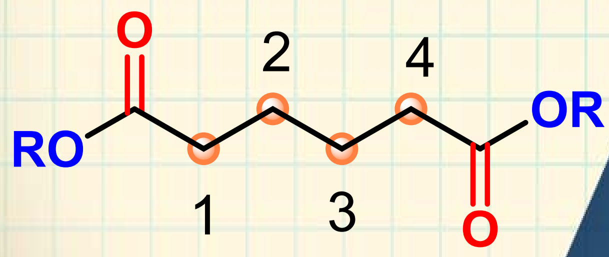




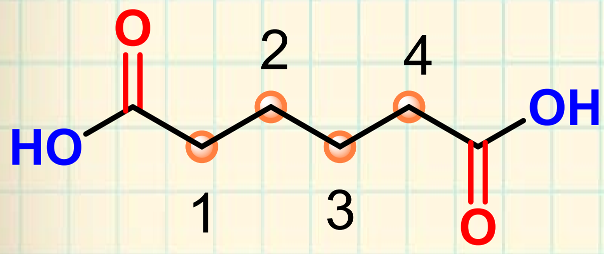
Routes to adipic acid (esters)

—— Carbonylation of 1,3-butadiene

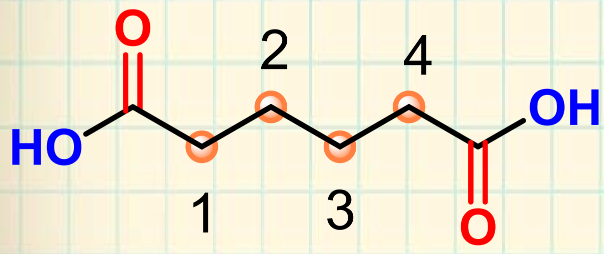
Reporter: Meng Wang

Supervisor: Dr. Ping Lu

Contents



Contents



Industry status

Global adipic acid demand

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

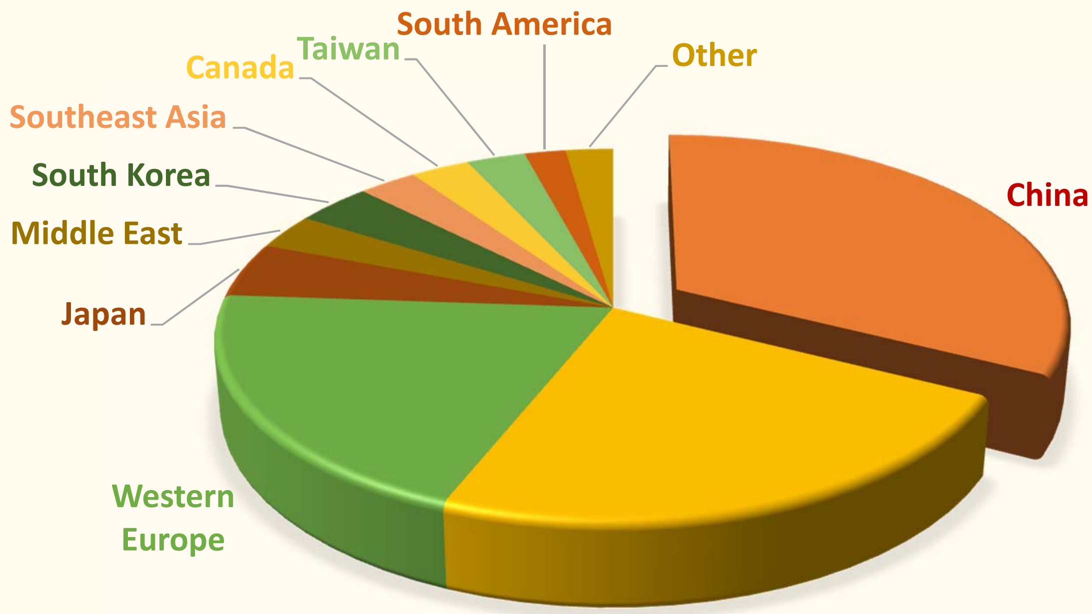
Asia adipic acid demand

- 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)

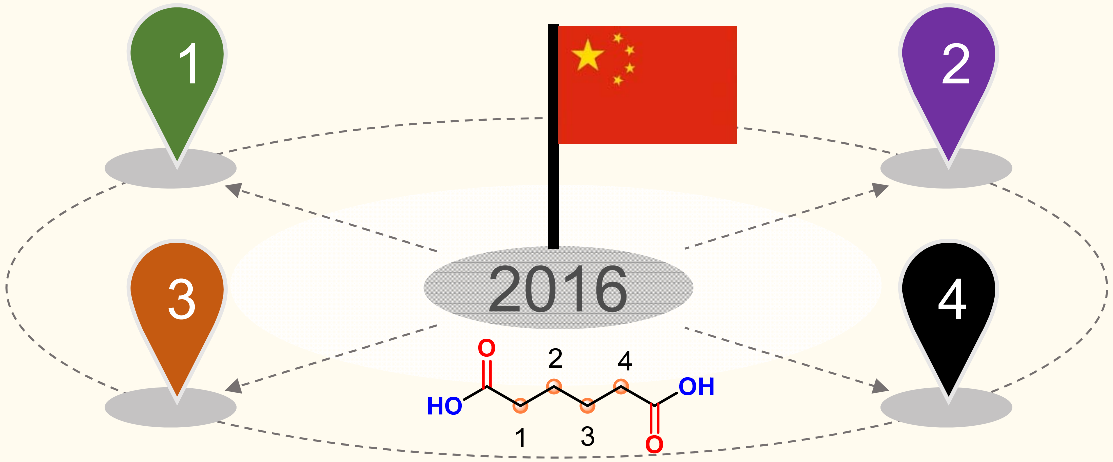


HIS Markit, May 2019

In terms of magnitude and growth, China leads the pack

total global capacity
~ 50%

global production
40%

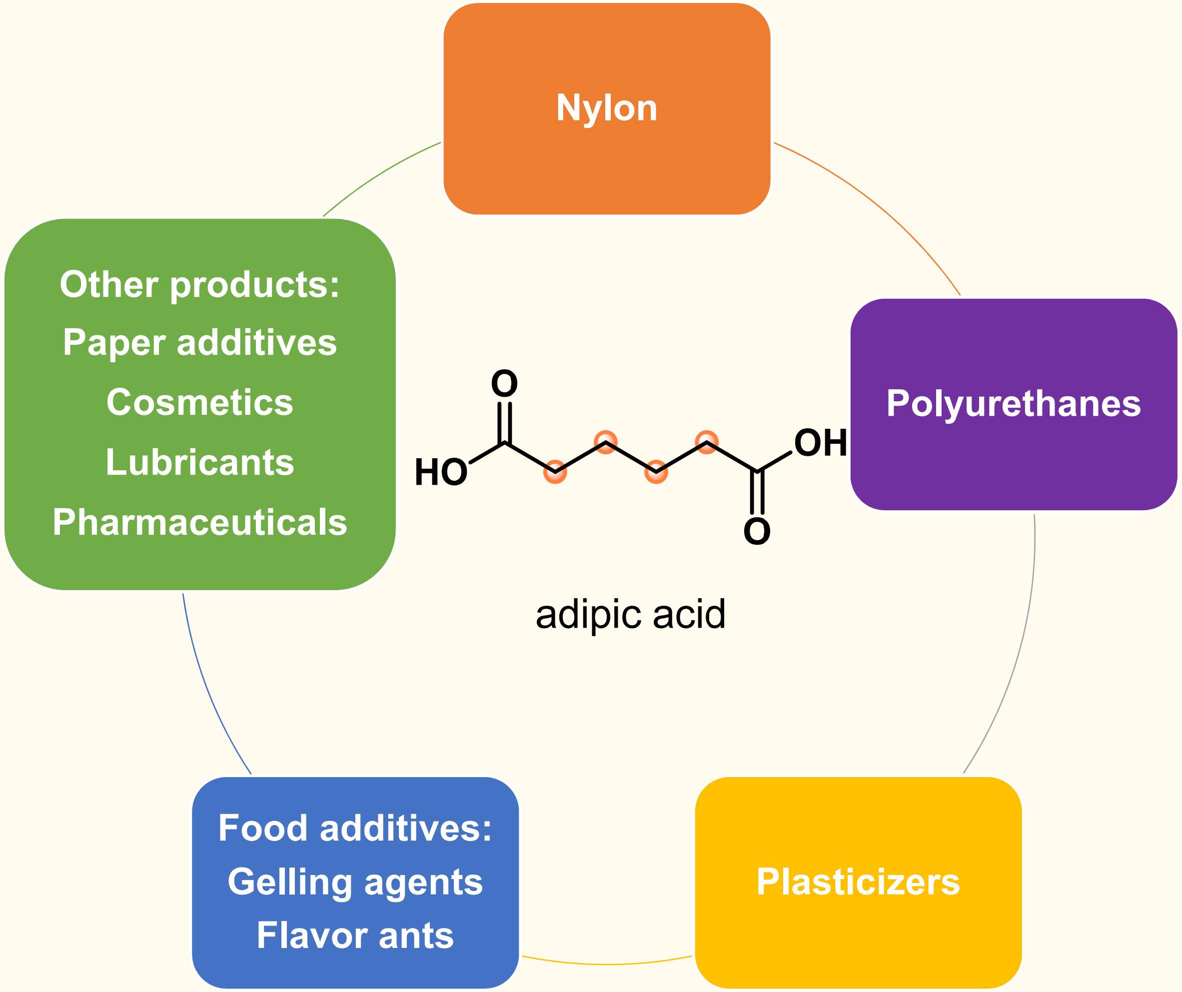


global consumption
30%

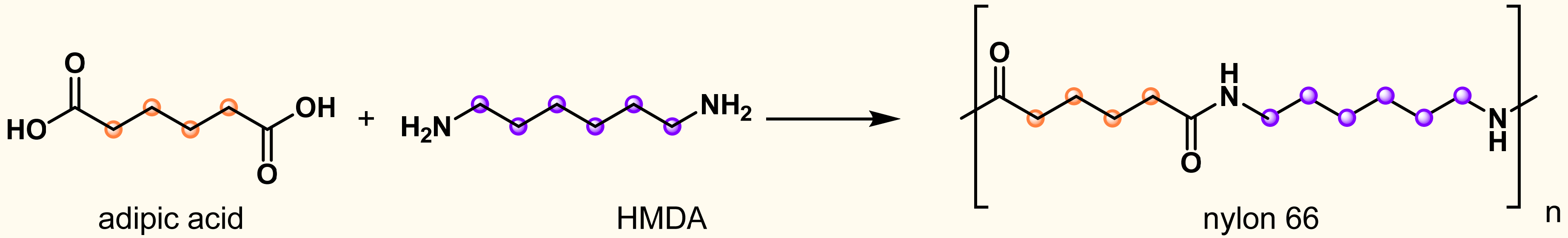
global export market
> 50%

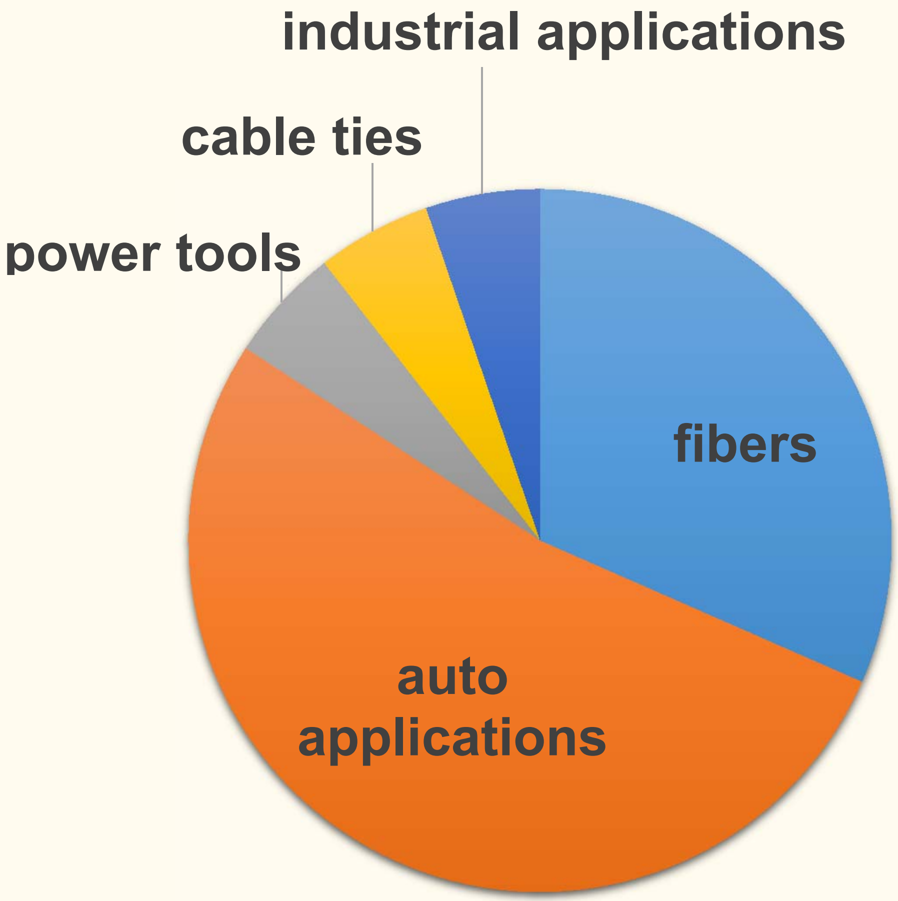
HIS Markit, May 2019

Adipic acid is used for?



The major market: a feedstock for nylon 66



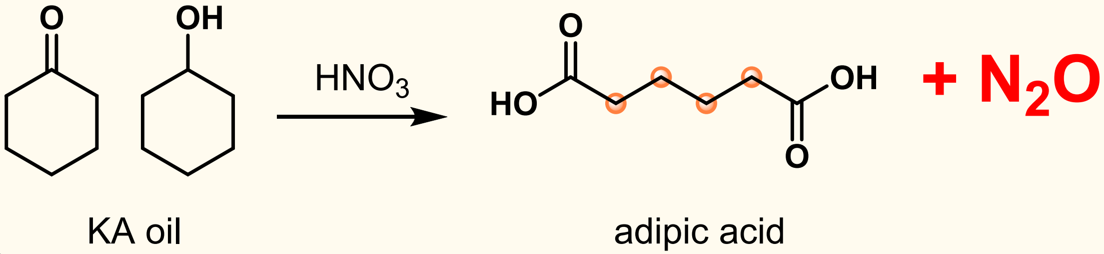


Nylon 66 will be the fastest-growing market for adipic acid in the forecasting period.

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

Problems existing in conventional way

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



N_2O
safety concerns
large investment
equipment corrosion

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

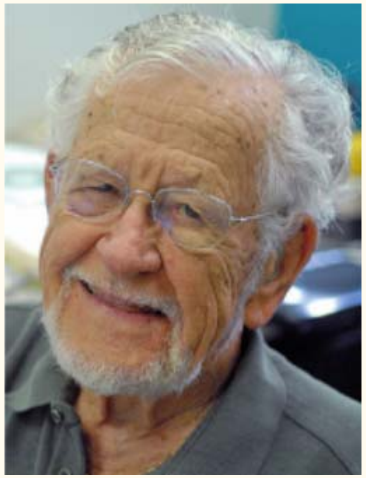
Barton Challenge: Adipic acid from n-hexane

——by Roberts, In Feb. 1998

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

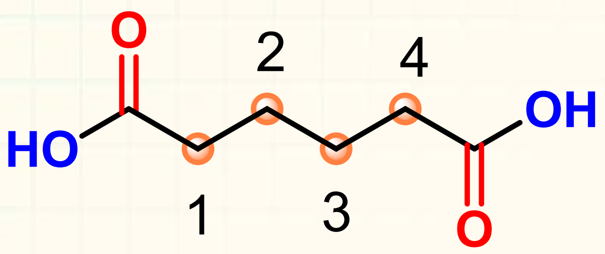
Purpose	In honor of Barton's groundbreaking research in selective oxidation of aliphatic and alicyclic hydrocarbons
Award	**$5,000**
Content	the first person or research group to produce adipic acid by a chemical or biochemical oxidation hexane with an 85% yield on the basis of hexane consumed

- 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.' "



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

Contents

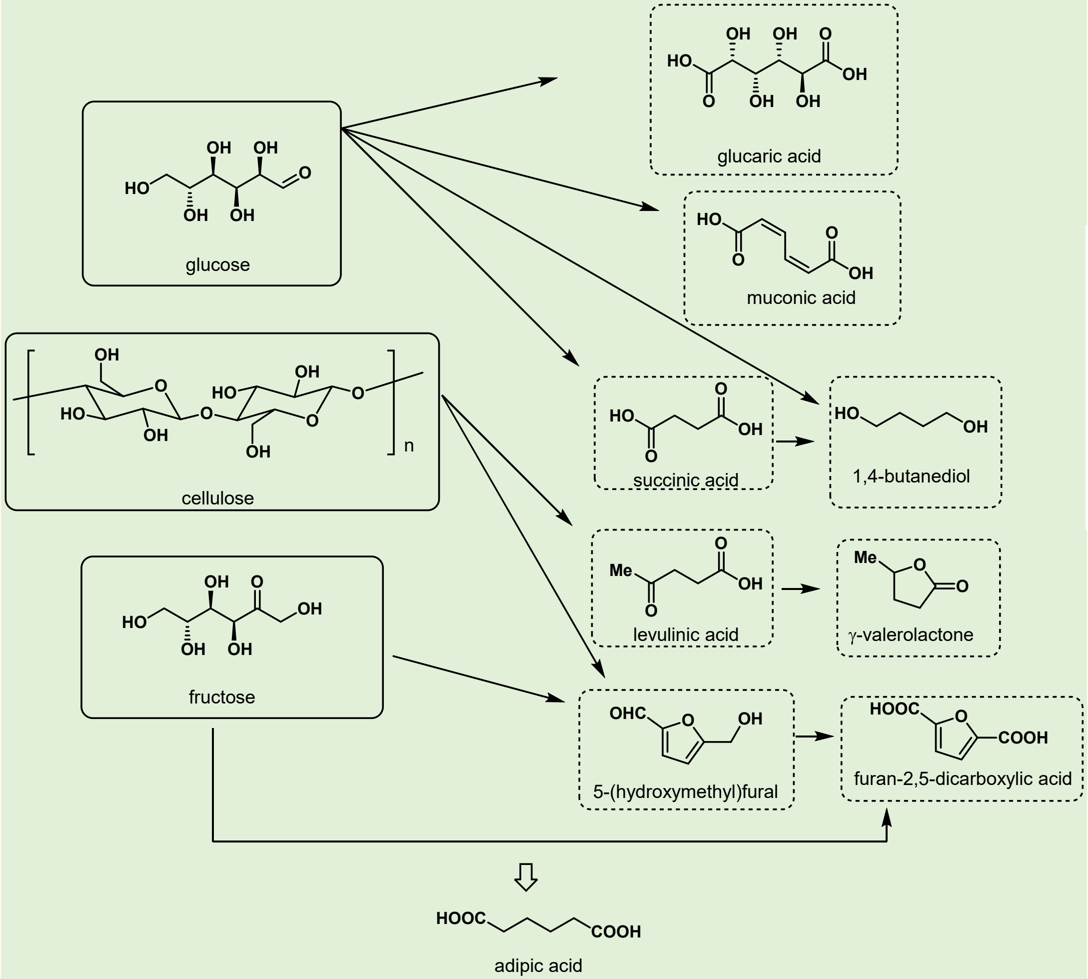


- The bio-based routes
- The petrochemical-based routes

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)

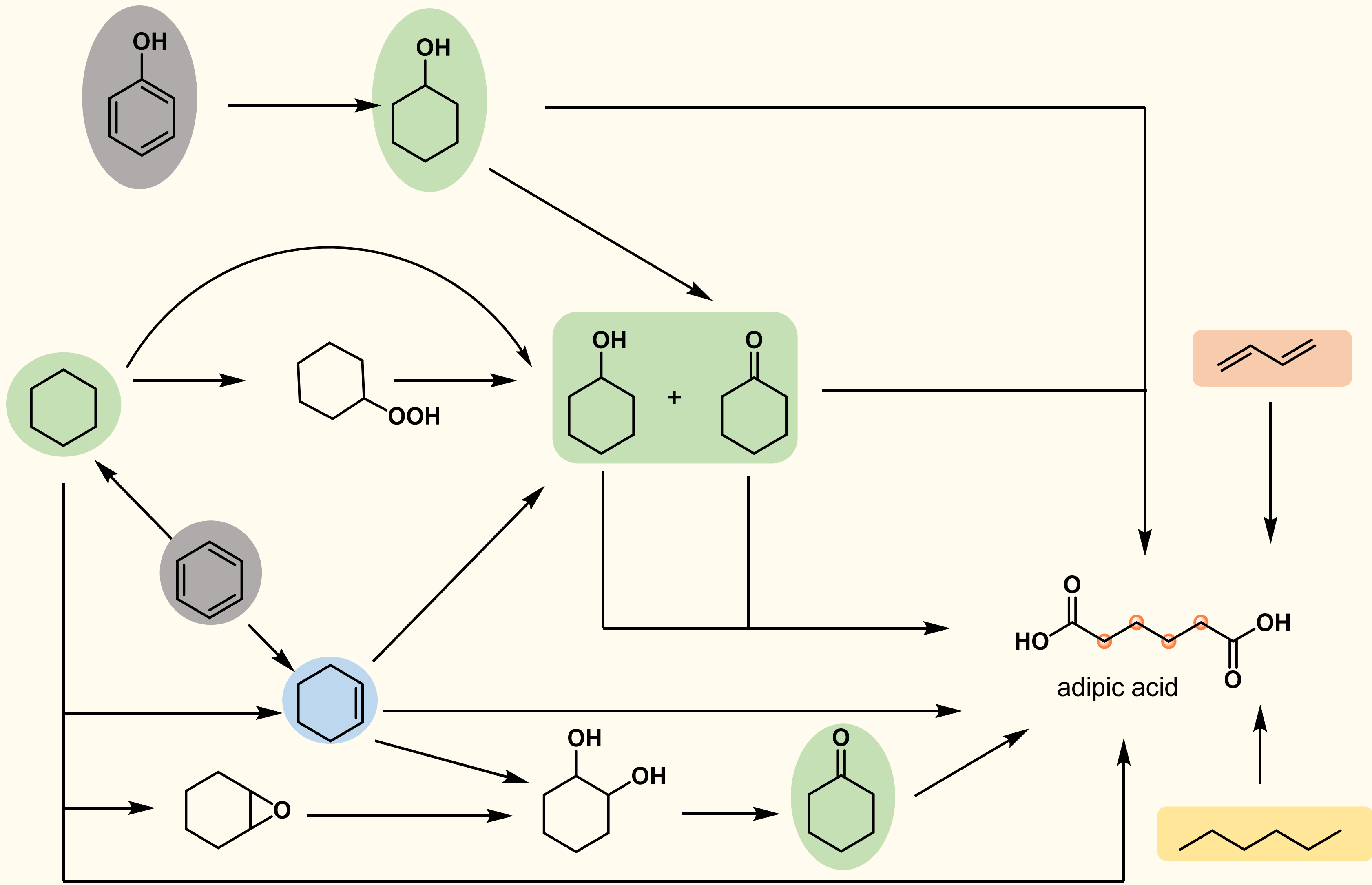


- ✓ **sustainable**
- ✓ **low production costs**
- ✓ **technology-specific market**

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

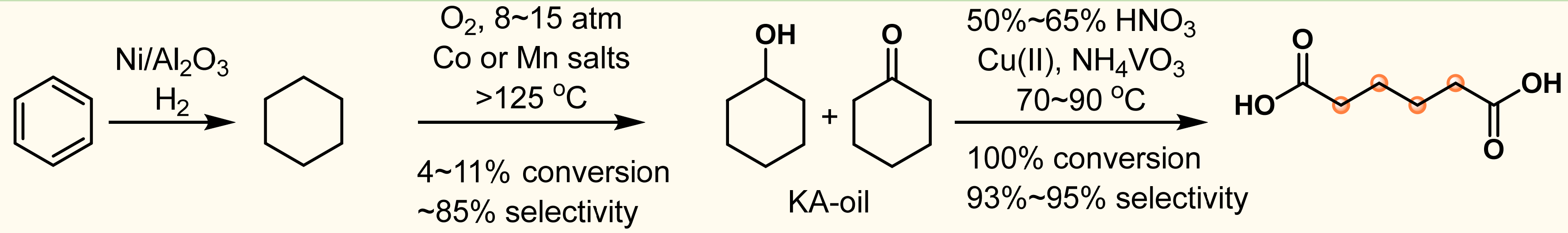


J. C. J. Bart, *Catal. Today* **1991**, *9*, 237
Applied Catalysis A: General **2001**, *211*,1

petrochemical-based routes: Industrial processes

From cyclohexane via cyclohexanone and cyclohexanol (KA oil)

—— the conventional process (by DuPont)

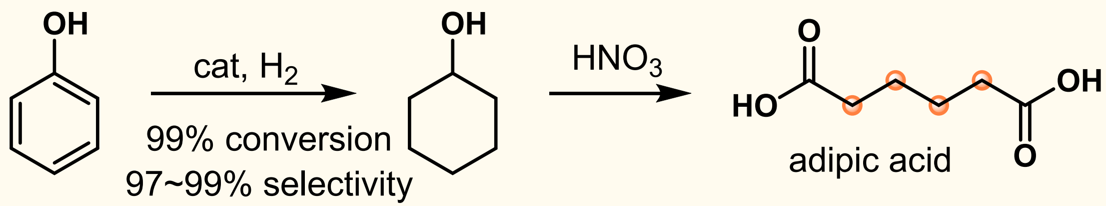


✓ mature
✓ economical efficiency

- 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

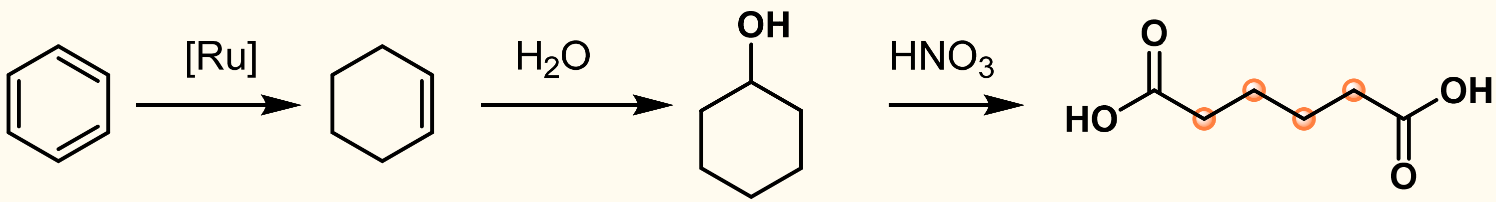
- environmental pollution
- large investment
- serious equipment corrosion
- safety concerns

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

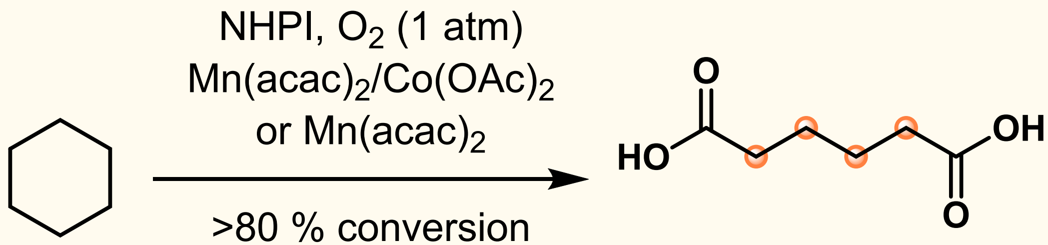
99% selectivity

- ✓ 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)



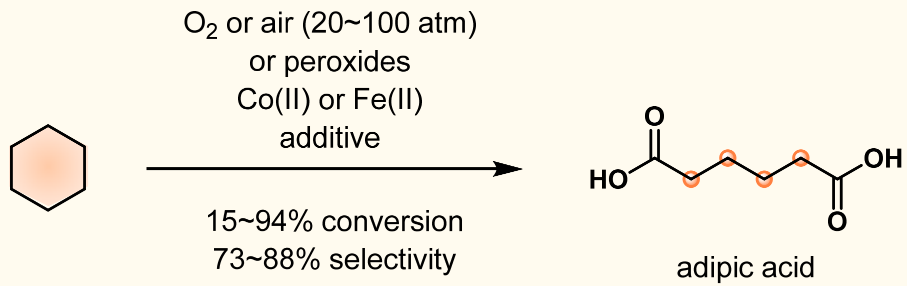
>80 % conversion
>76% selectivity

adipic acid

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

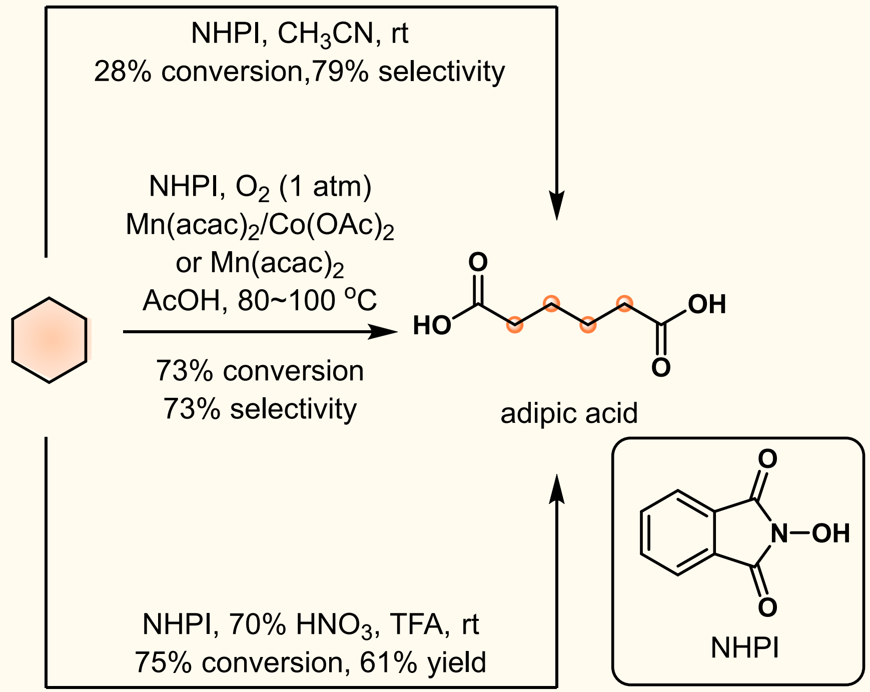
US Patent 4263453, **1981**
Japanese Patents 59184138, **1984**
R. J. Cicerone, *Nature* **1986**, *319*, 109
H. Nagahara and M. Konishi, *ibid*. **1987**, *62*, 45541
W. C. Trogler, *Science* **1991**, *251*, 932
P. E. Tomlinson, *Environ. Prog*. **1994**, *13*, 134
US Patent 5547905, **1996**
A. Scott, *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

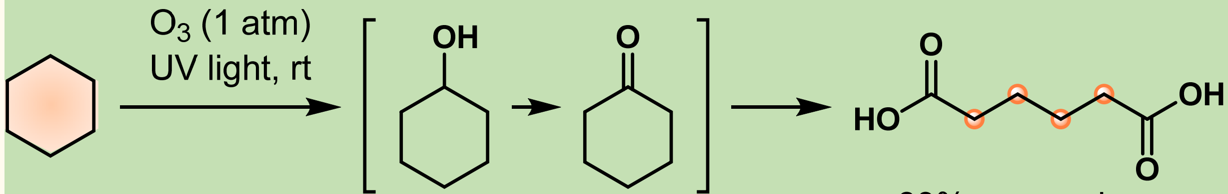
- ✓ **one step oxidation**
- ✓ **environmental friendly**
- **low conversion**
- **low selectivity**
- **additives**
- **tough conditions**



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

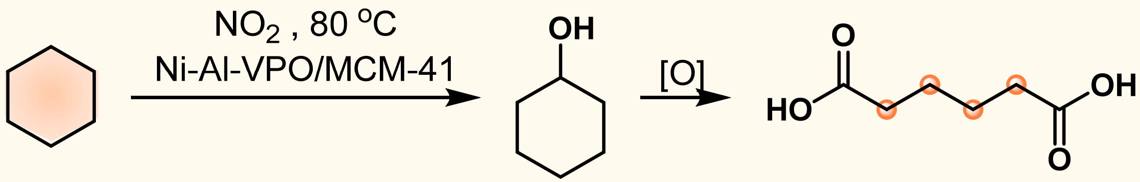


neat or + 8 vol% H_2O (0.5 M HCl)

83% conversion
90% selectivity

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

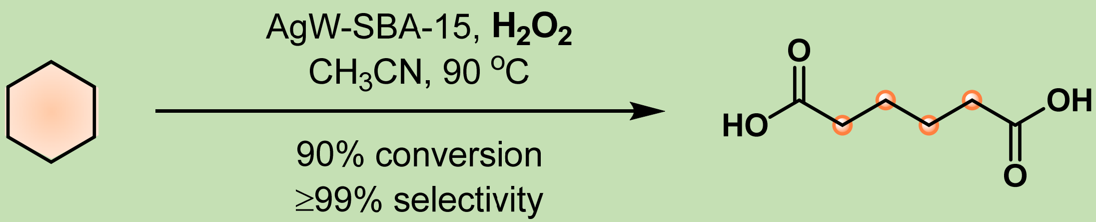
K. C. Hwang, *Science* **2014**, *346*, 1495



65% conversion
85% selectivity

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

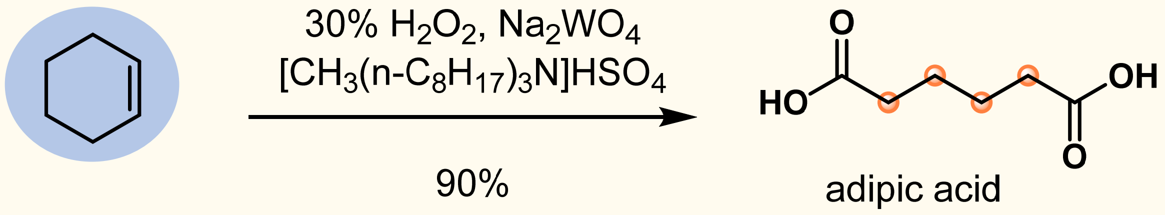
H. Luo, *Ind. Eng. Chem. Res*. **2016**, *55*, 3729



- ✓ 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



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

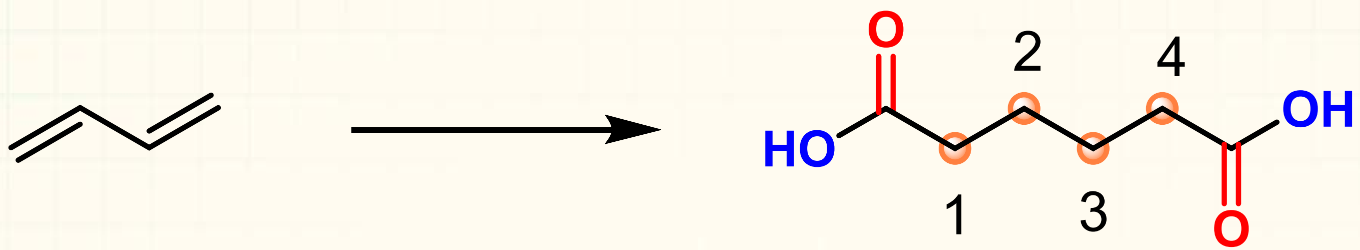
- ✓ one step oxidation
- ✓ less corrosive
- ✓ clean, safe, and reproducible
- • expensive systems
- • PTC- environmental pollution

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