Sonochemistry

By colin hughes

Outline

- Introduction, background
- Beginnings of sonochemistry
- How it works
- Specific reactions
- Why certain reactions are helped and others are not

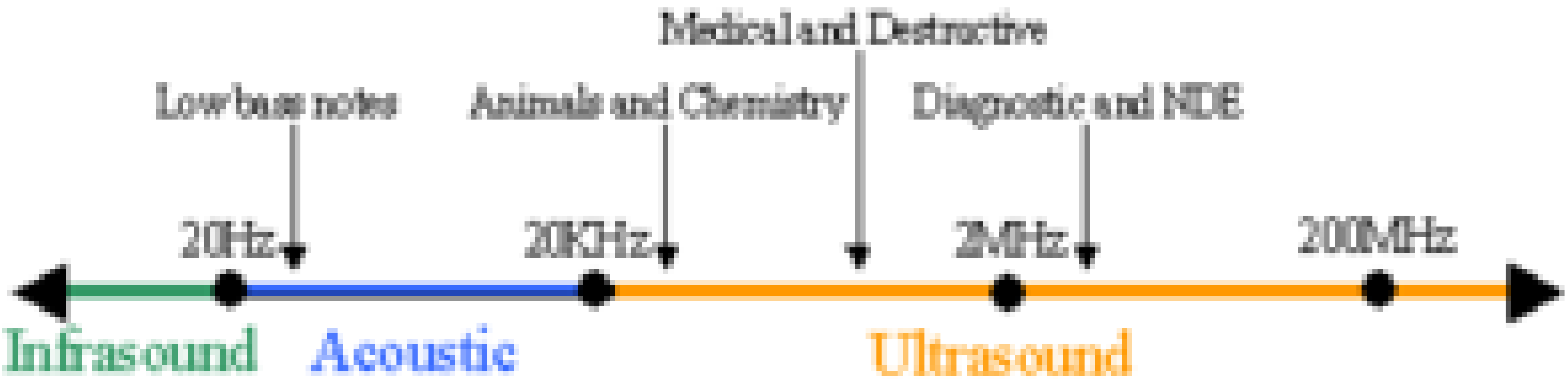
)) (( ))))) US

Brief introduction to sonochemistry

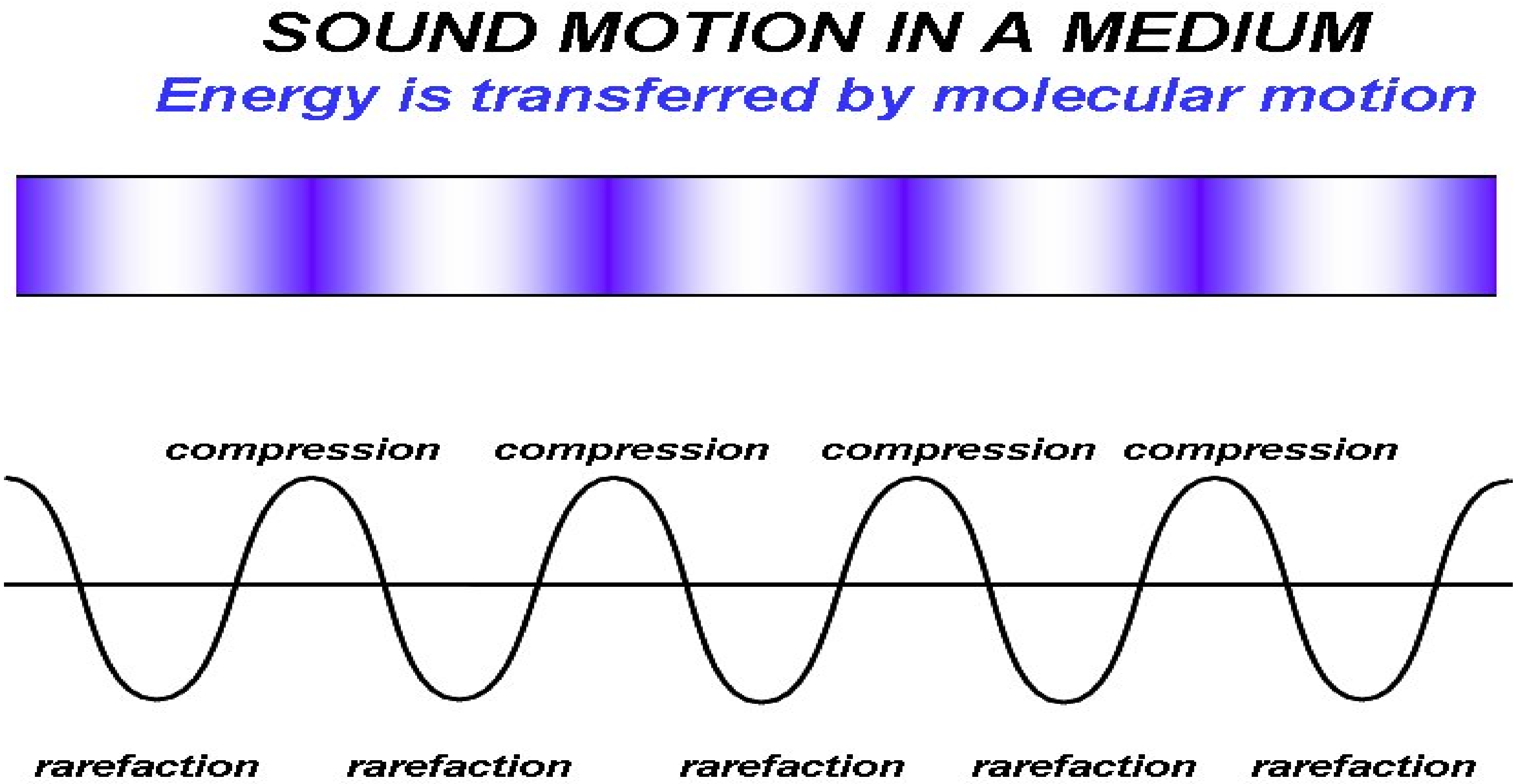
- Enhances reaction rates up to a million times
- Believed to be due to small cavities (100 microns) which implode, creating tremendous heat and pressure, shock waves, and particle accelerations. This process is called "**cavitation**"
- Started gaining attention for organic chemists when someone noticed that organic solvents formed cavities

What is ultrasound?

- Name of sound with frequency above normal human hearing, 20kHz
- BTW, sound is waves of compression and expansion moving through a medium



A short review of sound



Common uses

- Alarms
- Dog whistles
- Tooth brushes
- Cleaners
- Medical uses
- Allows bats to hunt insects
- Cell phone ring tones for teenagers (old people can’t hear the phones ringing)
- Detecting submarines

Sonochemistry, destroyer of destroyers

- During the testing of torpedo boats in 1894 the British noticed severe vibrations of the ships along with erosion of the propellers
- They also noticed large bubbles, or cavities, from spinning propellers
- Simple solution: larger propellers and slower rotation

But the boats got bigger

- Boats got bigger, and the problem got worse
- Lord Rayleigh (NP 1904) was asked to investigate
- He confirmed bubbles imploding on the surface of the propellers was to blame. He also blamed bubbles for the sound a tea kettle makes when water starts to boil
- The effect was named “cavitation”

Before & After-pictorial proof

Shiny new Francis turbine

Turbine destroyed by cavitation

1927-beginning of intercontinental flight and sonochemistry

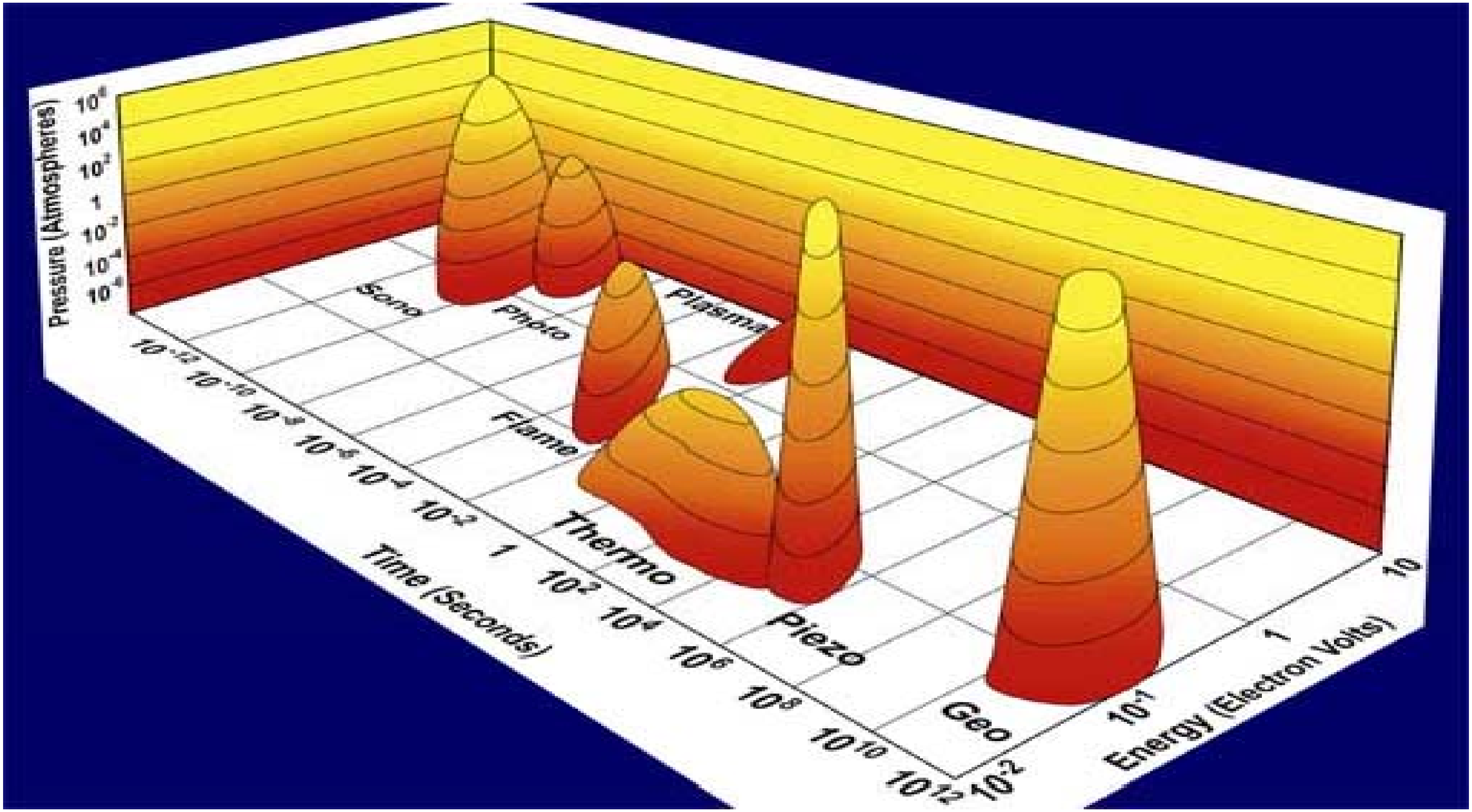
- Loomis reported beneficial uses of ultrasound to chemistry, such as
  - Ever so slightly depressing boiling points
  - Increasing the rate of the Iodine clock reaction
  - Expulsions of supersaturated dissolved gasses
  - Increases in the rate of hydrolysis of dimethyl sulfate

JACS 49, 3086

Why it is special to chemists

- Sonochemistry involves high energies and pressures on a short time scale
- Photochemistry interacts with chemicals on short time scale at high energies, thermochemistry interacts on a long time scale at lower energies

A chart to illustrate

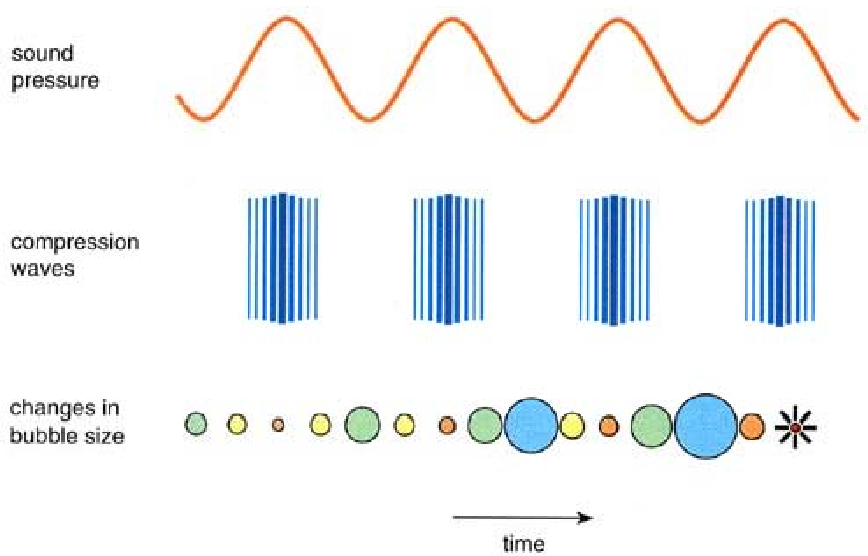


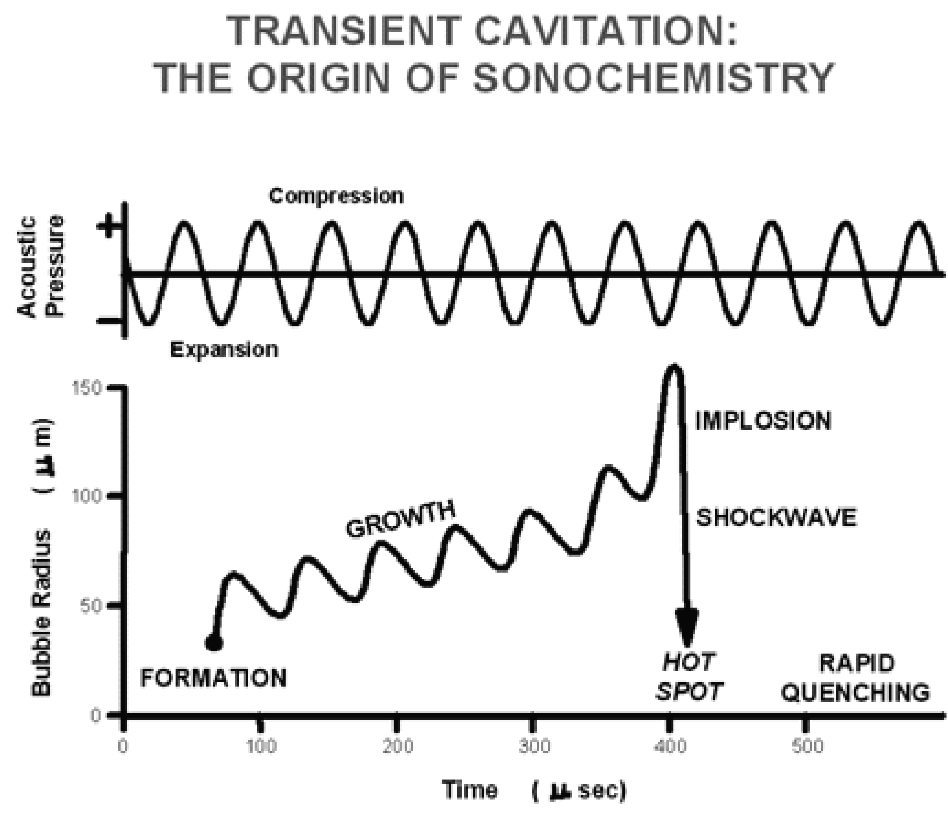
How cavities are formed

- Tensile strengths of liquid important
- When negative pressure exceeds tensile strength of liquid, cavities form
- Nucleated process; without weak points, ultrasound could not form cavities
- Dissolved gasses often help for cavities, as tensile strength is weakened
- Every solvent forms cavities, not just water

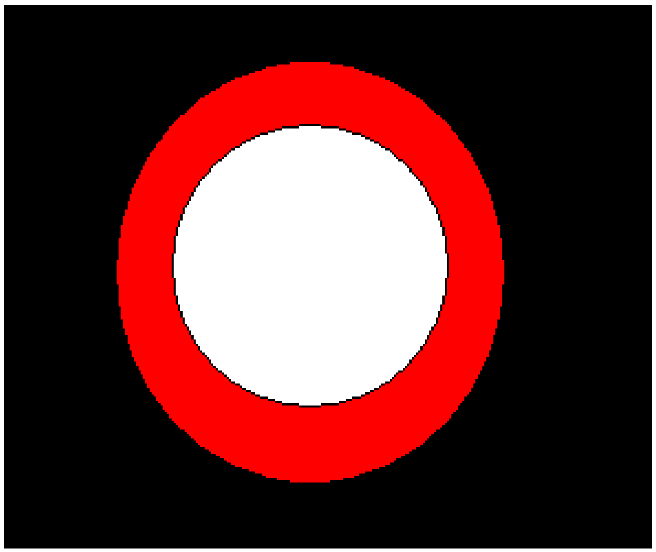
J. Phys. Chem. A **2006** *110,* 10720

Rectified diffusion

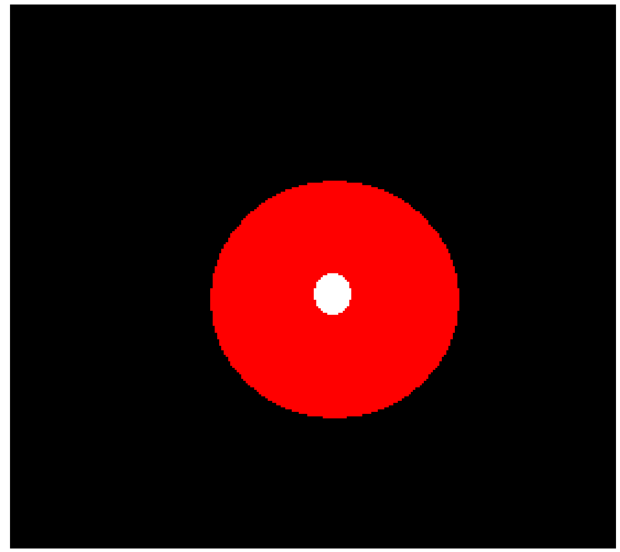




Cavitation and hot spots



Cavity

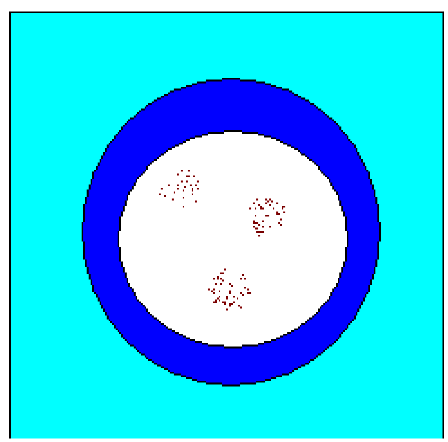


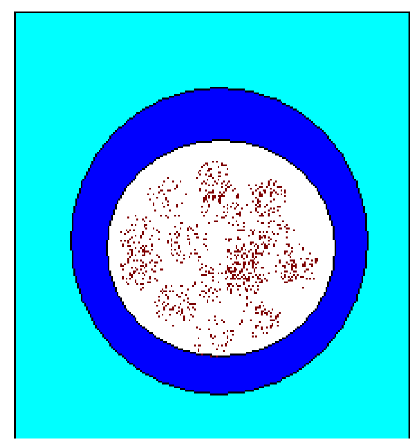
Imploding cavity

Black: bulk liquid, ambient temperature
Red: supercritical fluid 1900 º K
White: cavity with some gas 5000 º K

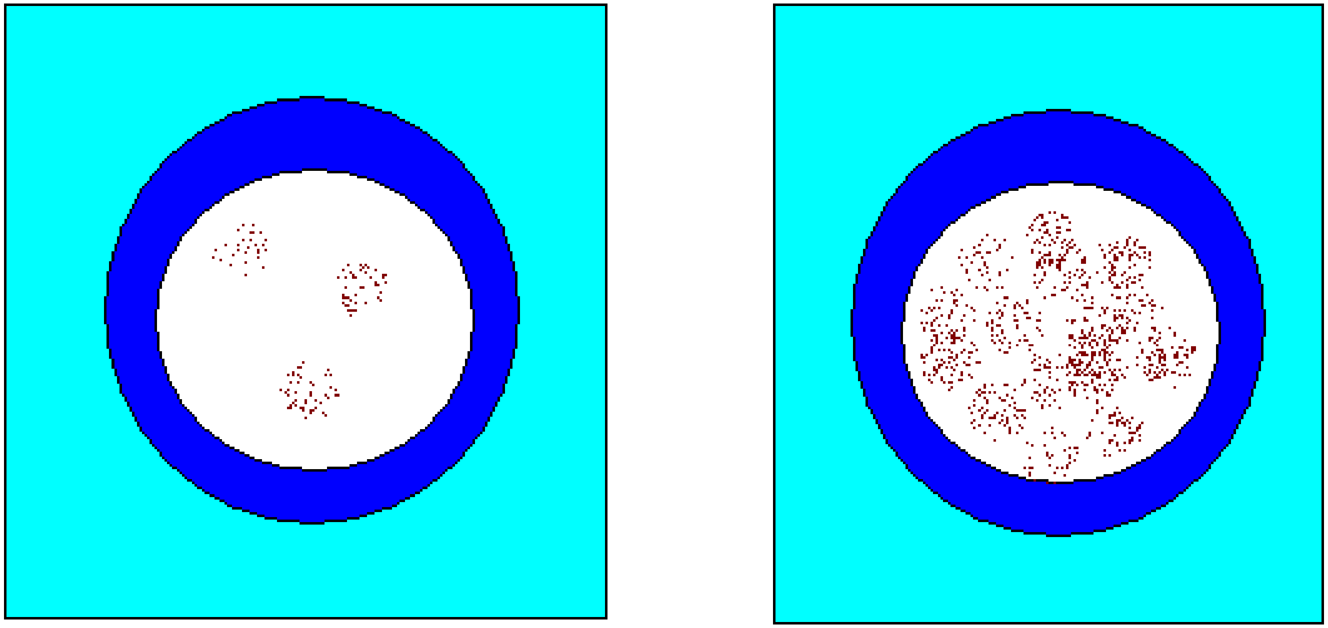
Solvent and temperature effects

- More void the cavity, the hotter it becomes upon collapse
- Vapor pressure important
  - Lower vapor pressure solvents lead to hotter cavitation
  - Lower temperature solvents foster hotter cavitation





Filled cavities



Aqua blue: bulk liquid
Blue: supercritical fluid
White: cavity
Magenta dots in cavity: gas

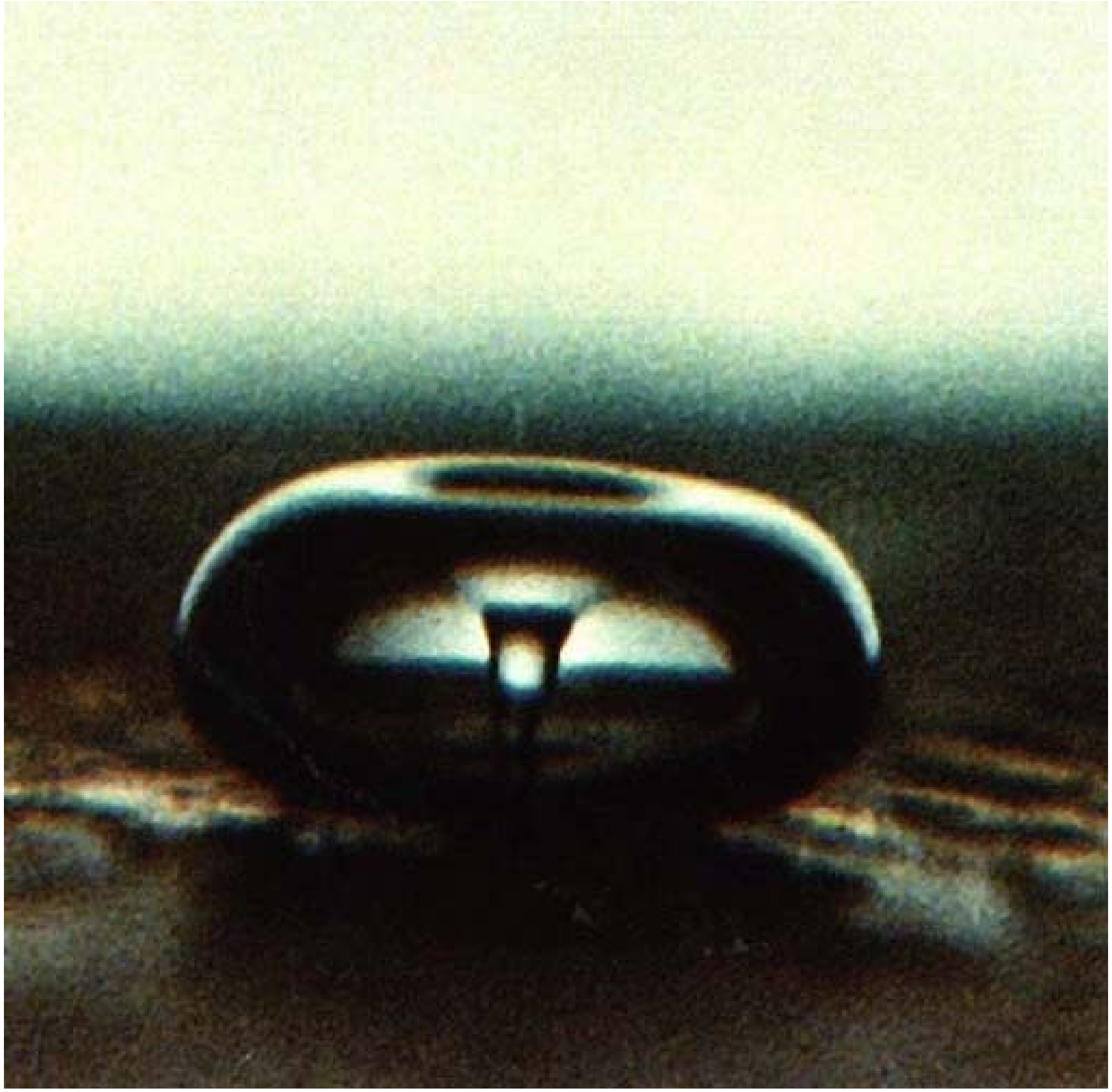
What we can learn from this

- Do your sonication experiments cold
- If deciding between two solvents, go with the higher boiling
- If you want to super-charge your reaction, bubble some Xe through the solution, as it transfers heat fairly terribly

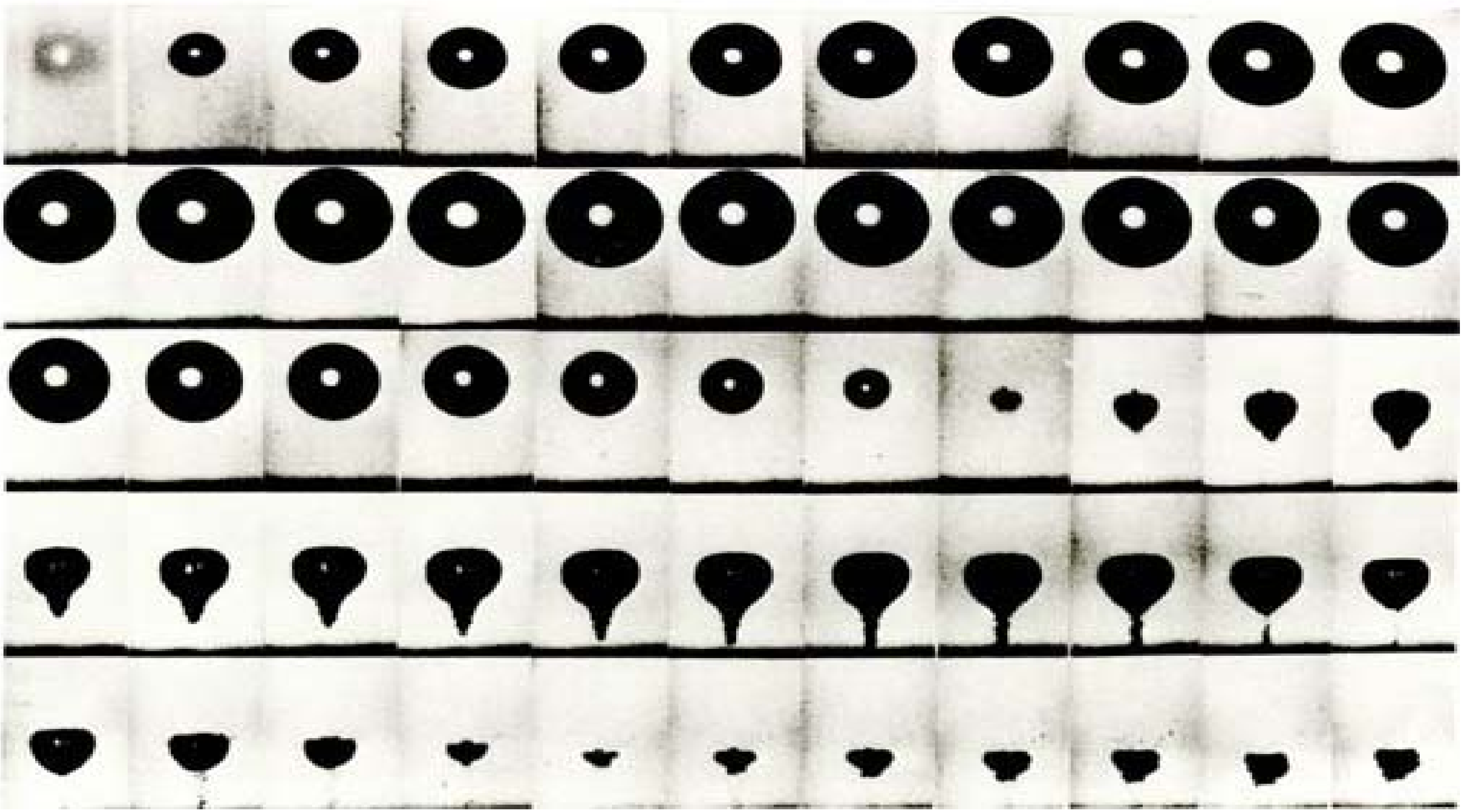
Cavitation with large solids present

- With solids present, collapsing bubbles change
- No longer symmetric, they deform, resulting in hot jets of liquid directed towards the solid
- Effects: removes oxidized outer layer
- THIS IS HOW CLEANING WORKS

Jet of hot liquid shooting towards a metal



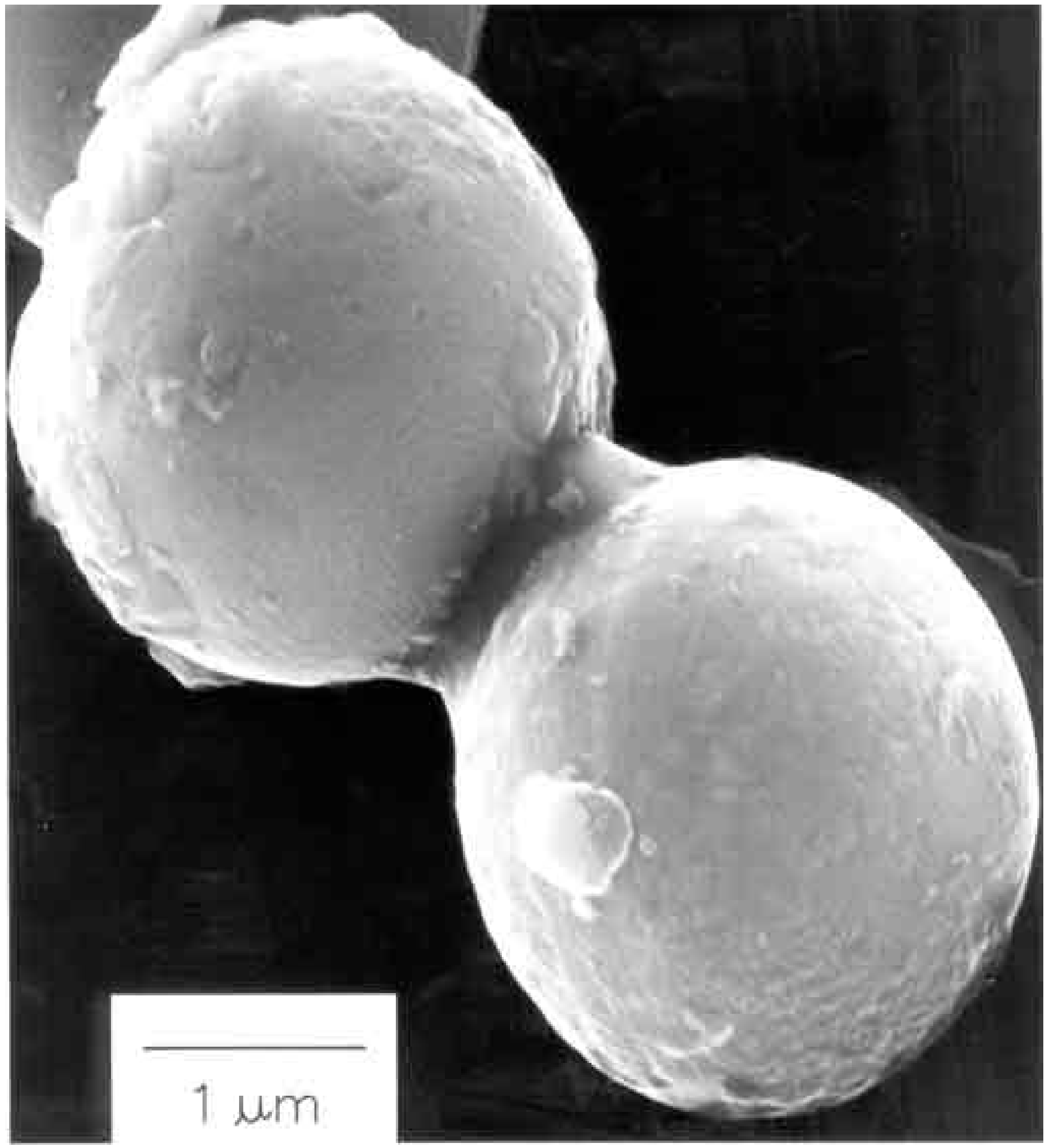
Still action shot



Small metals

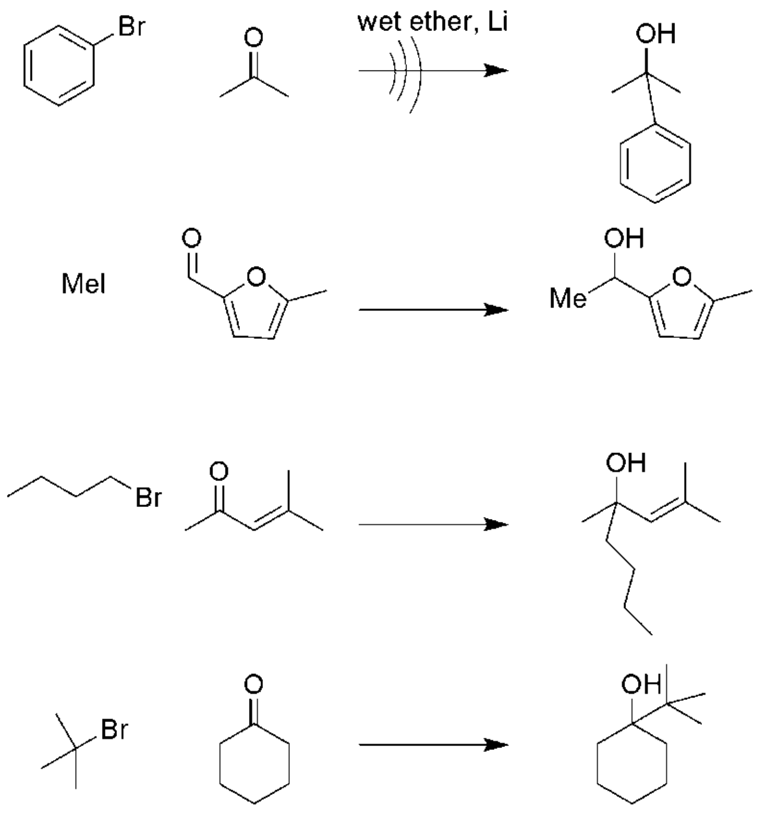
- Metal particles on the order of bubbles won’t produce hot jets
- Shock waves propel metals at really fast speeds, which can collide with other metals
- By understanding and manipulating pchem, Suslick and coworkers determined that these collisions can attain temperatures of 3,000k

Zinc fused from sonicated collisions



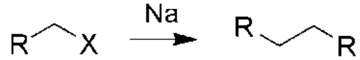
Ken Suslick's vanity plate

Barbier reaction



reaction time m	yield %
30	100
10	100
15	100
30	78

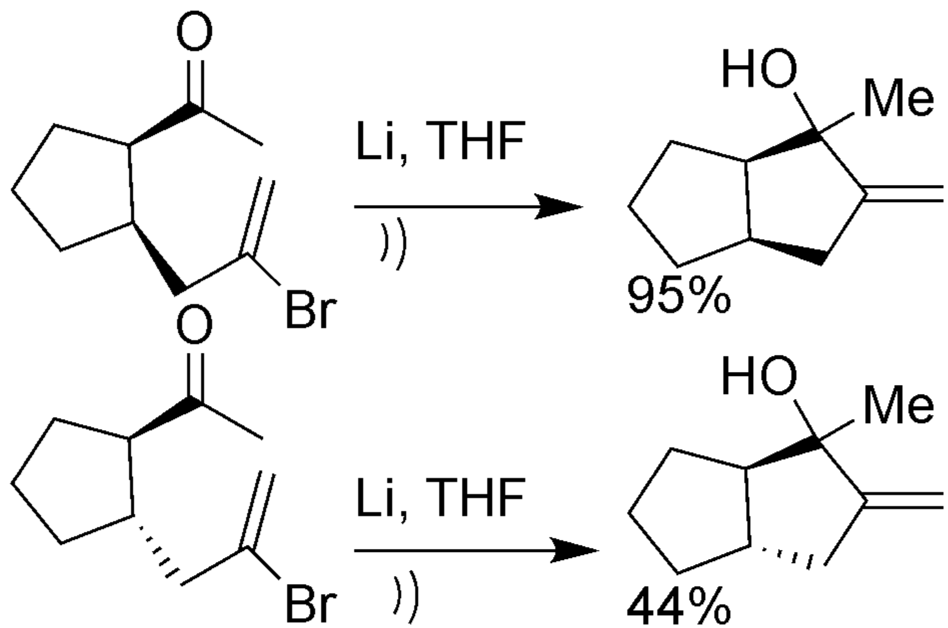
no Wurtz coulpling products observed



Wurtz coupling

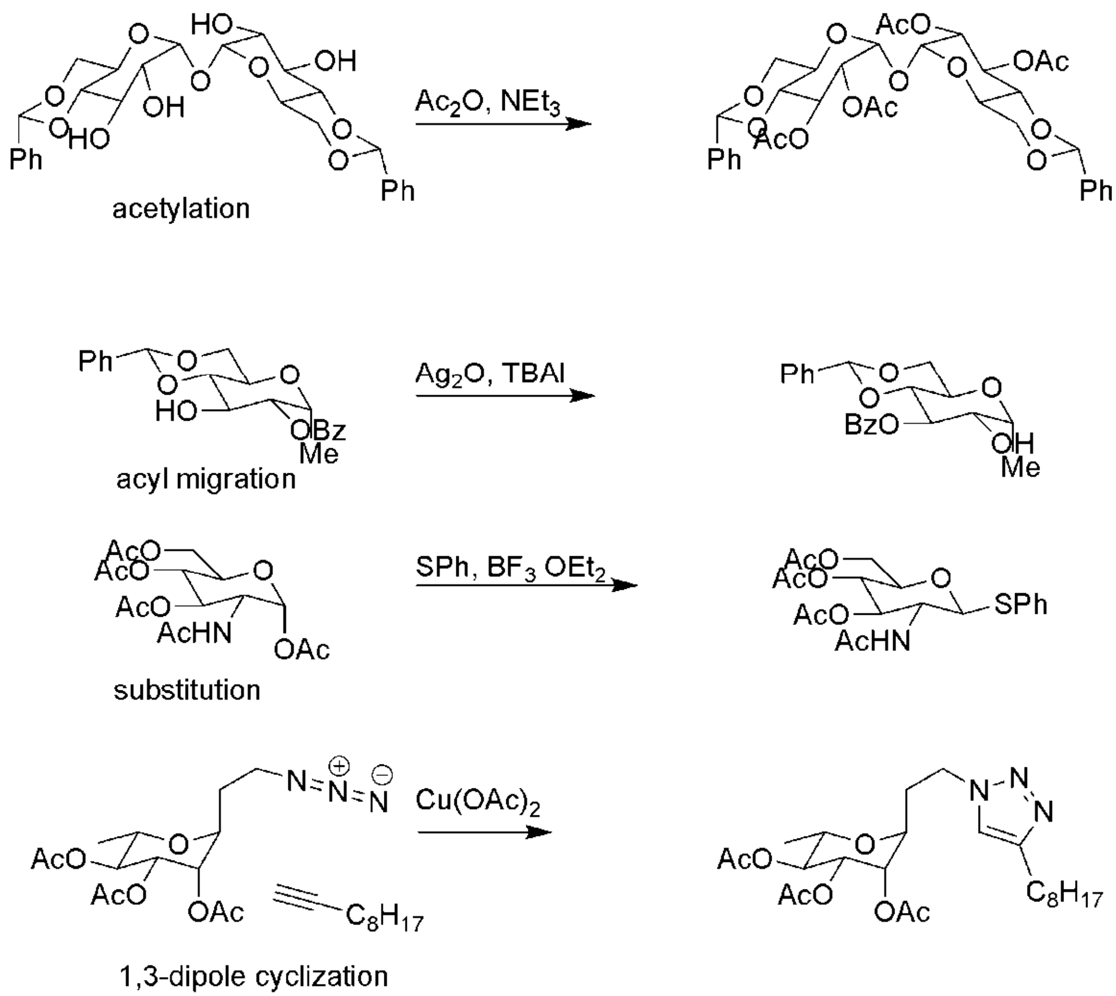
JACS 102, 7926

Trost experiments



JACS 104, 6879

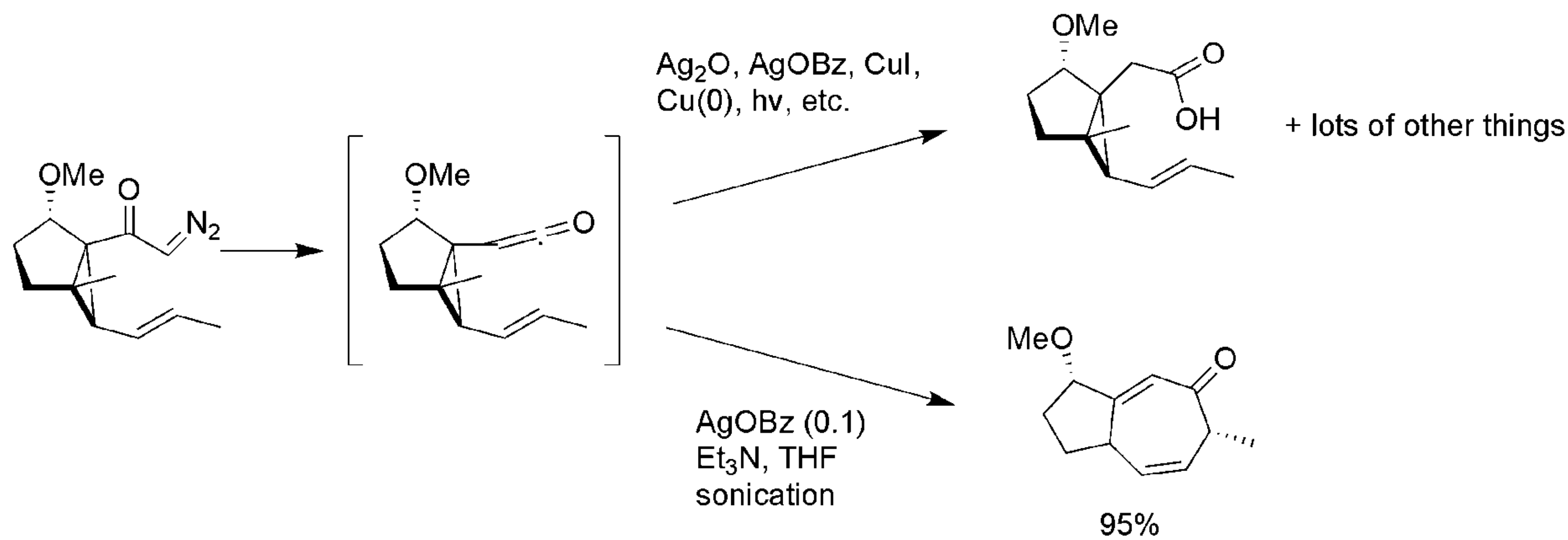
Biochemical applications



sonocation	without
92% 9m	bad, long
72% 5m	bad, days
83% 120 m	a week
98% 10 m	days

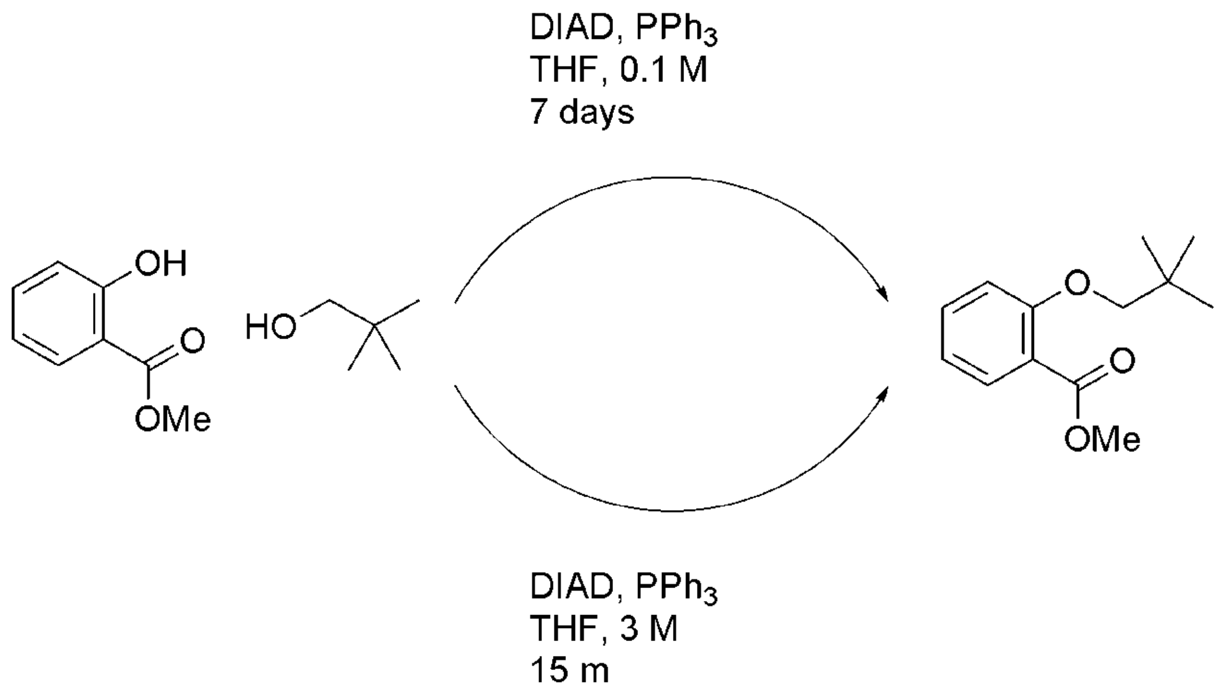
JOC 71, 5179

Tandem Wolff-Cope



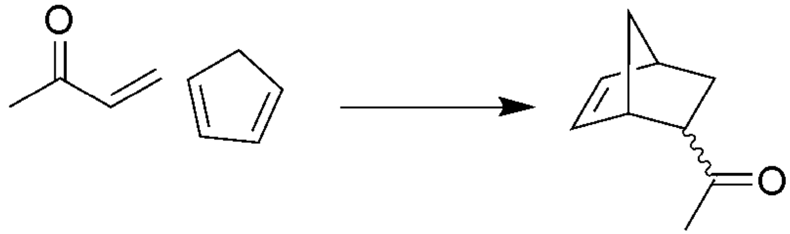
JACS 126, 24   JACS 125, 13624

Dramatic reduction in hindered Mitsunobu reaction rate

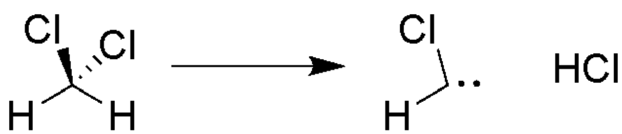


JOC 68, 8261

Apparent US effect in halogenated solvents actually not that cool



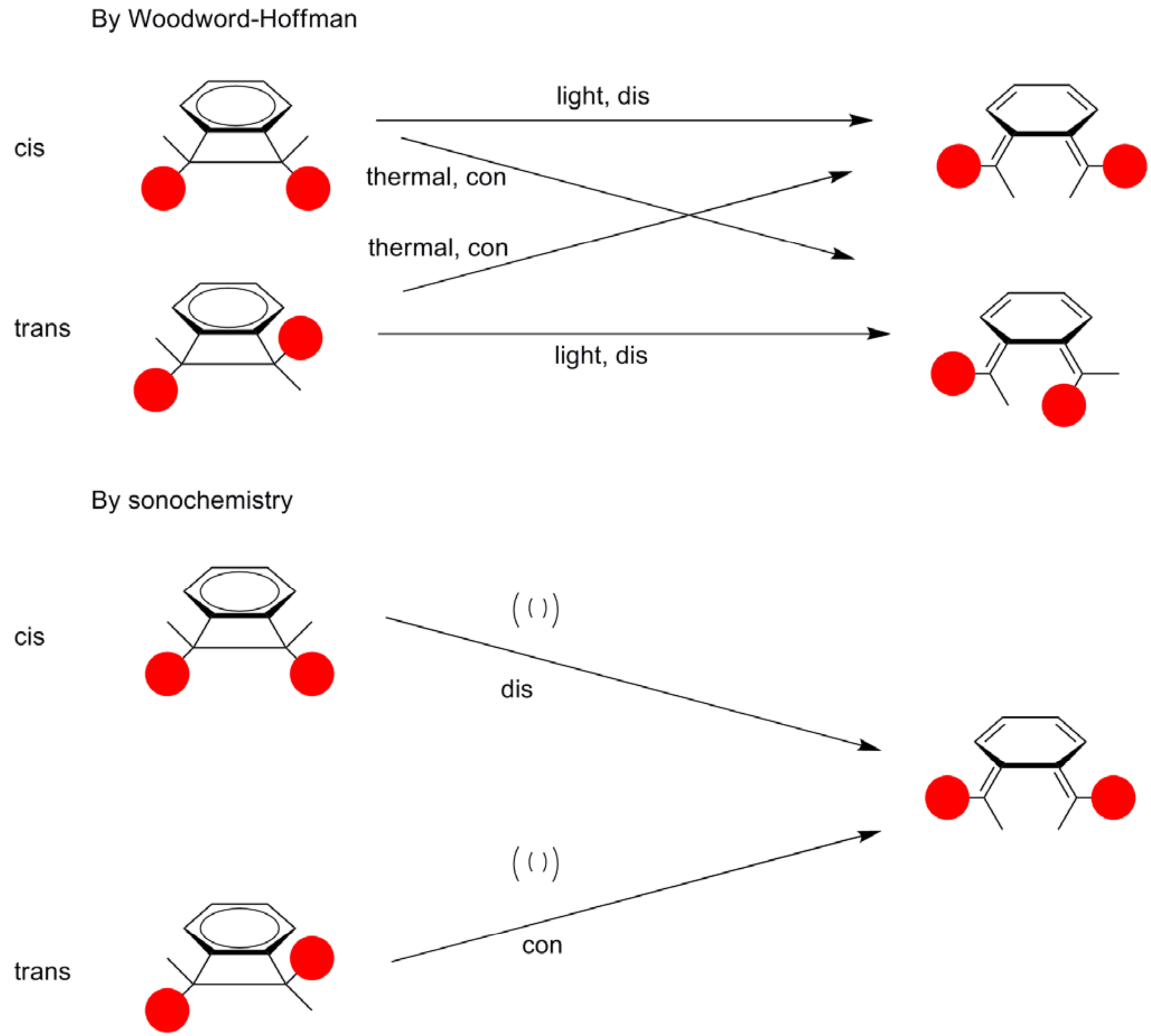
solvent	ultrasound	without
	yield (%)	
toluene	3	3
CH_2Cl_2	18	4



When HCl gas bubbled in, results were identical to sonication

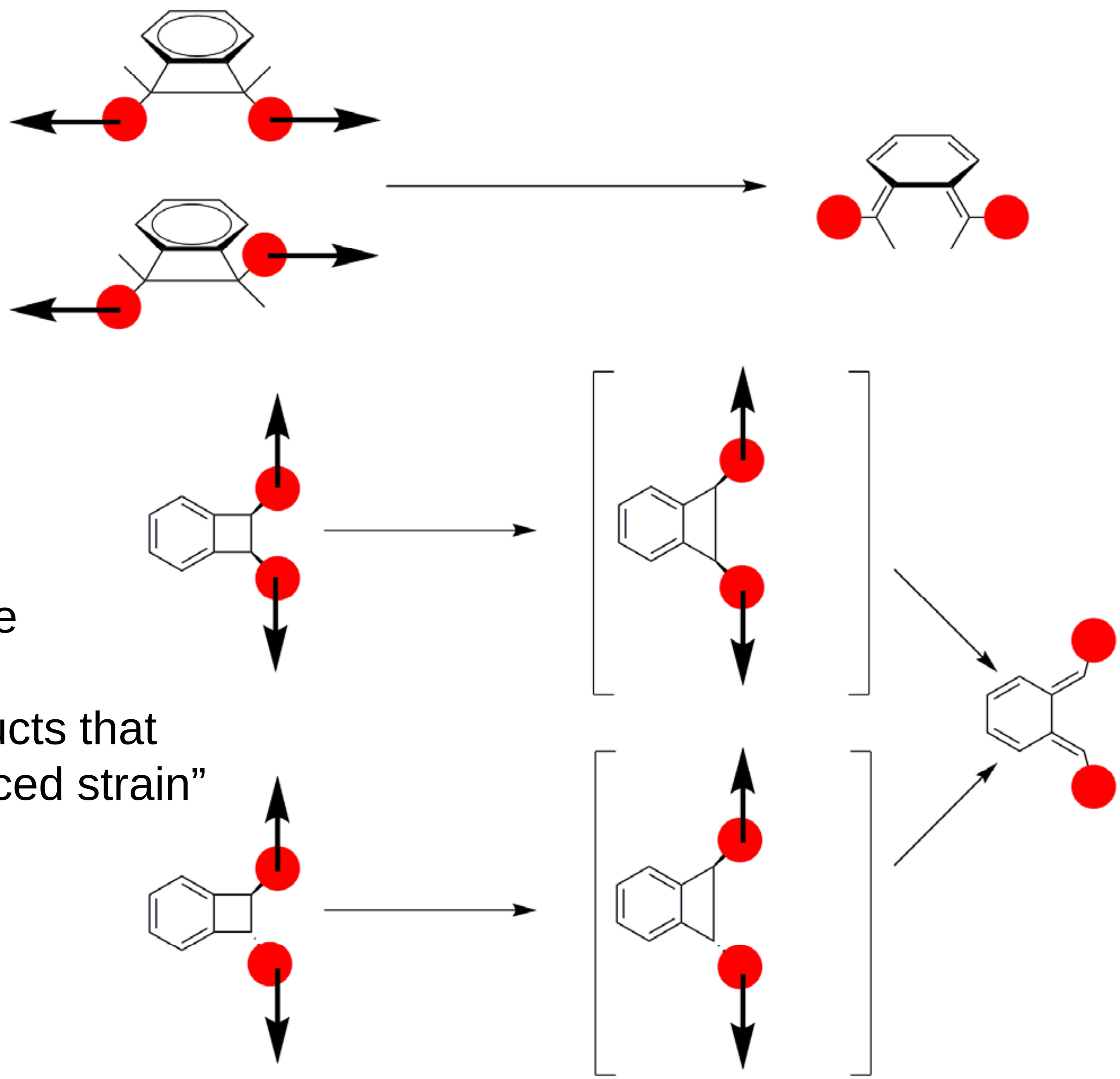
JOC 61, 2547

What about Bob (Woodward)?



Nature, 446, 423

Stress: not just for grad students

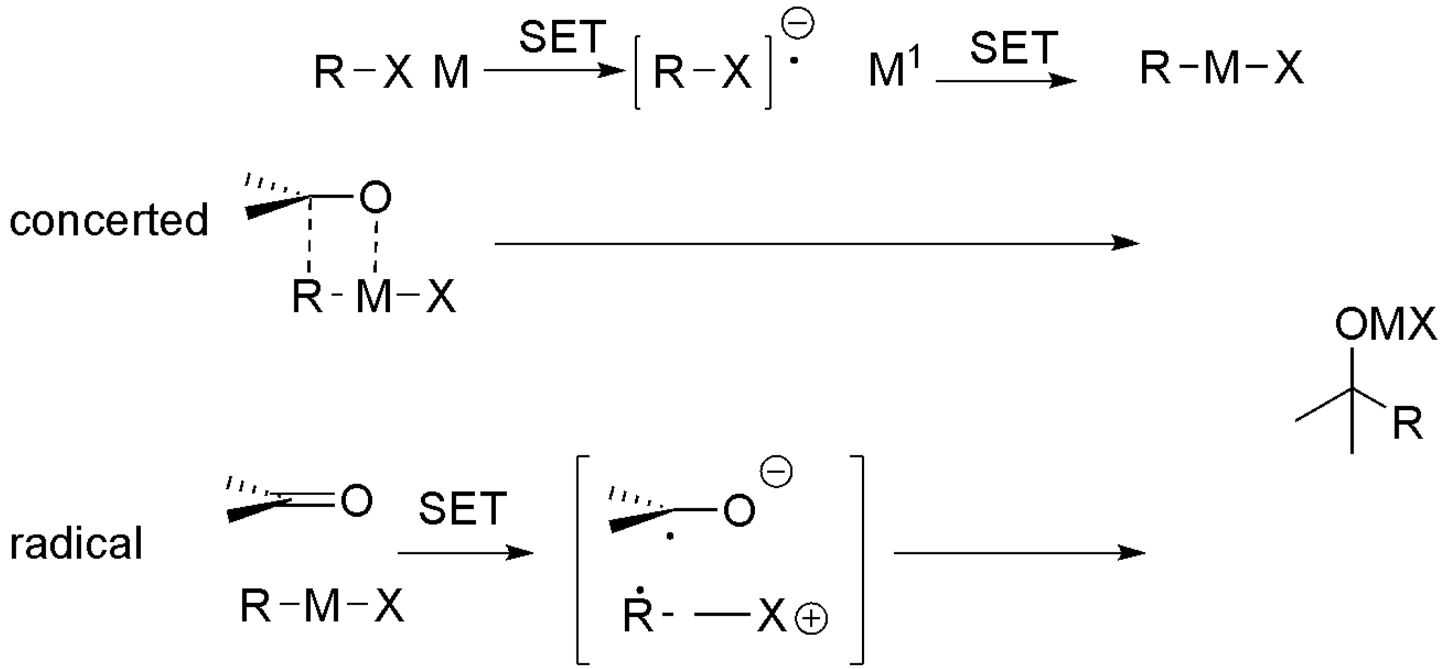


“mechanical force
biases reaction
pathway to products that
best relieve induced strain”

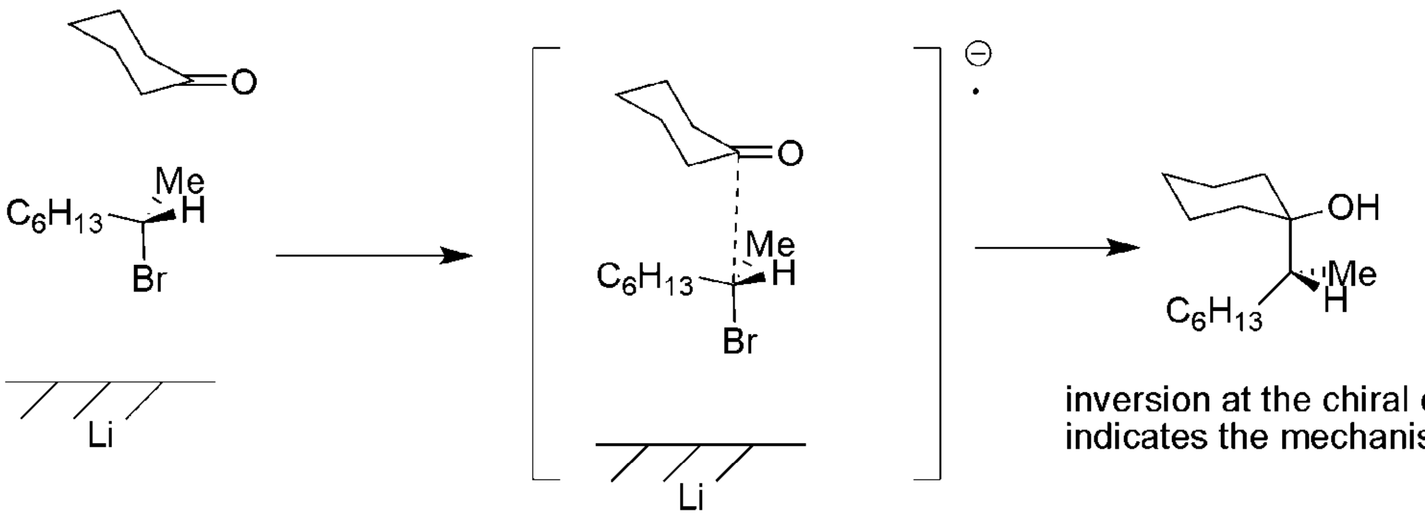
We also need Bull.Soc. Chim. Fr. II

- Chanon published a paper in 1985 according to which “sonication should be able to modify significantly electron transfer processes”

Two possibilities of Barbier coupling



Luche shows SET pathway



inversion at the chiral center
indicates the mechanism shown

Tet. Lett. 31, 7619;   Tet. Lett. 29, 4125

Luche develops a new interpretation

- Luche classified organic sonochemical reactions by types
- Heterogeneous reactions were sped up due to mechanical effects of the sound waves (agitation, cleaning effects)
- Homogeneous reactions were sped up due to generation of radicals
- "true" sonochemical reactions are those which involve a SET

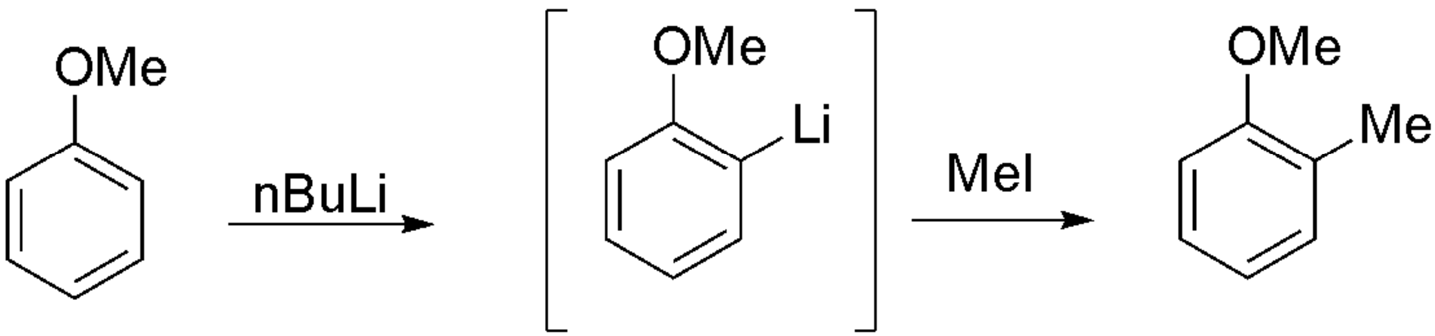
Tet. Lett. 29, 4125

How to prove it?

- Probe homogeneous reactions known to have NO radical character with US and without
- Probe substrates known to proceed to product via radical and ionic mechanism. Termed sonical “switching”

- If he is correct he would have opened a door to improving many reactions
  - HWE
  - Cannizzaro
  - Cope

Testing US with known anionic reactions

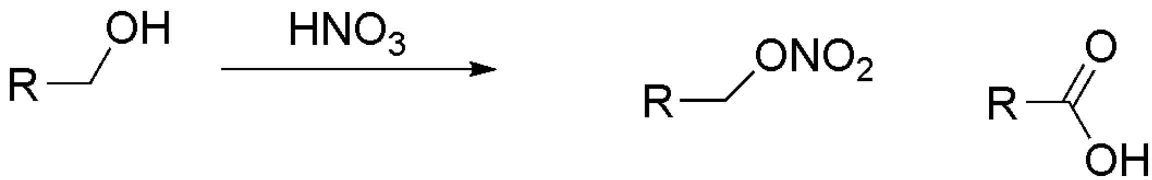


Known to react purely via anionic mechanism

Ultrasound had no effect on rate or yield (score one for Luche)

Tet. Lett. 29, 4129

Switching



without US	100%	0%
with US	0%	100%

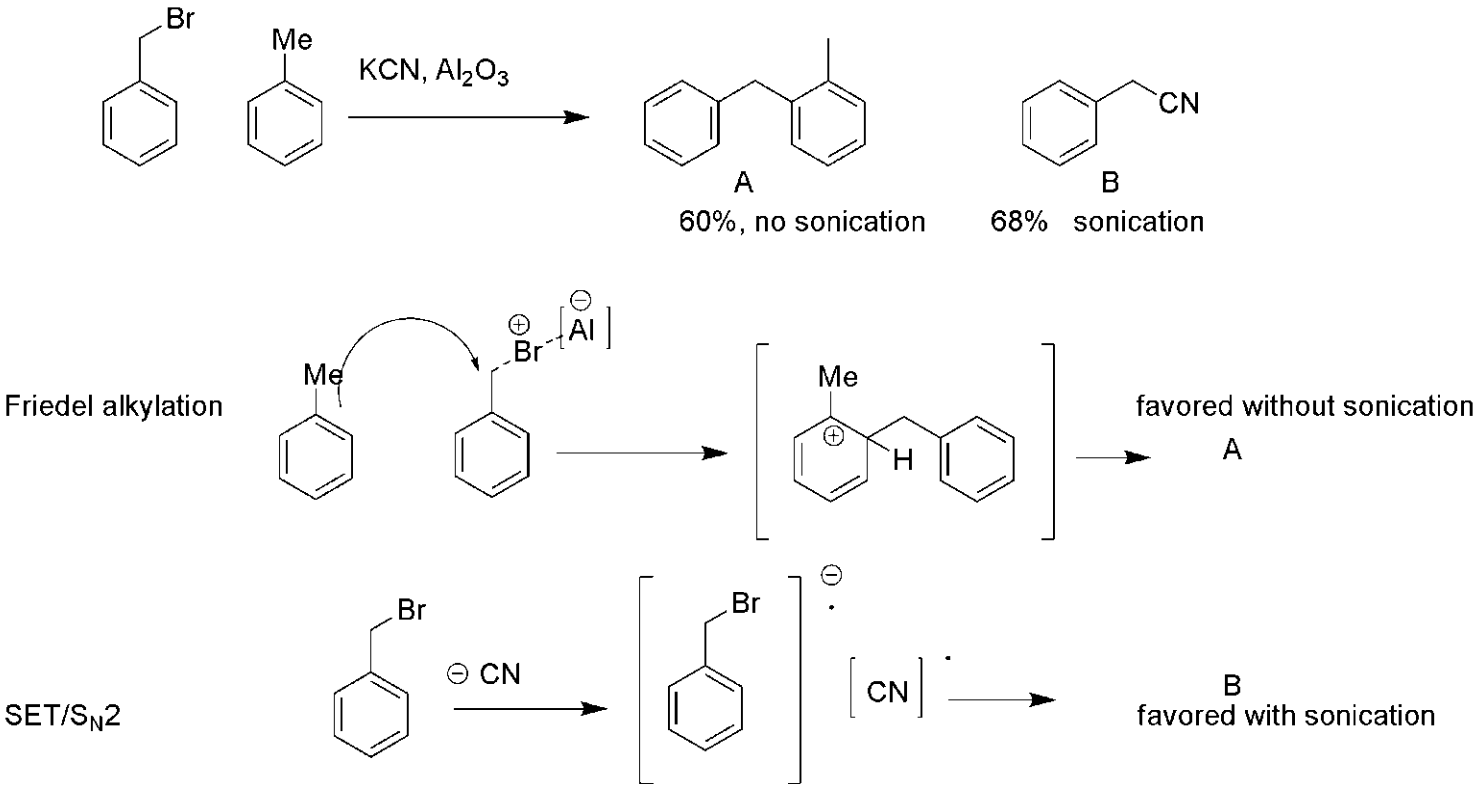
reaction to the acid known to proceed through a radical cation

reaction to the nitrate ester known to proceed purly via ionic mechanism

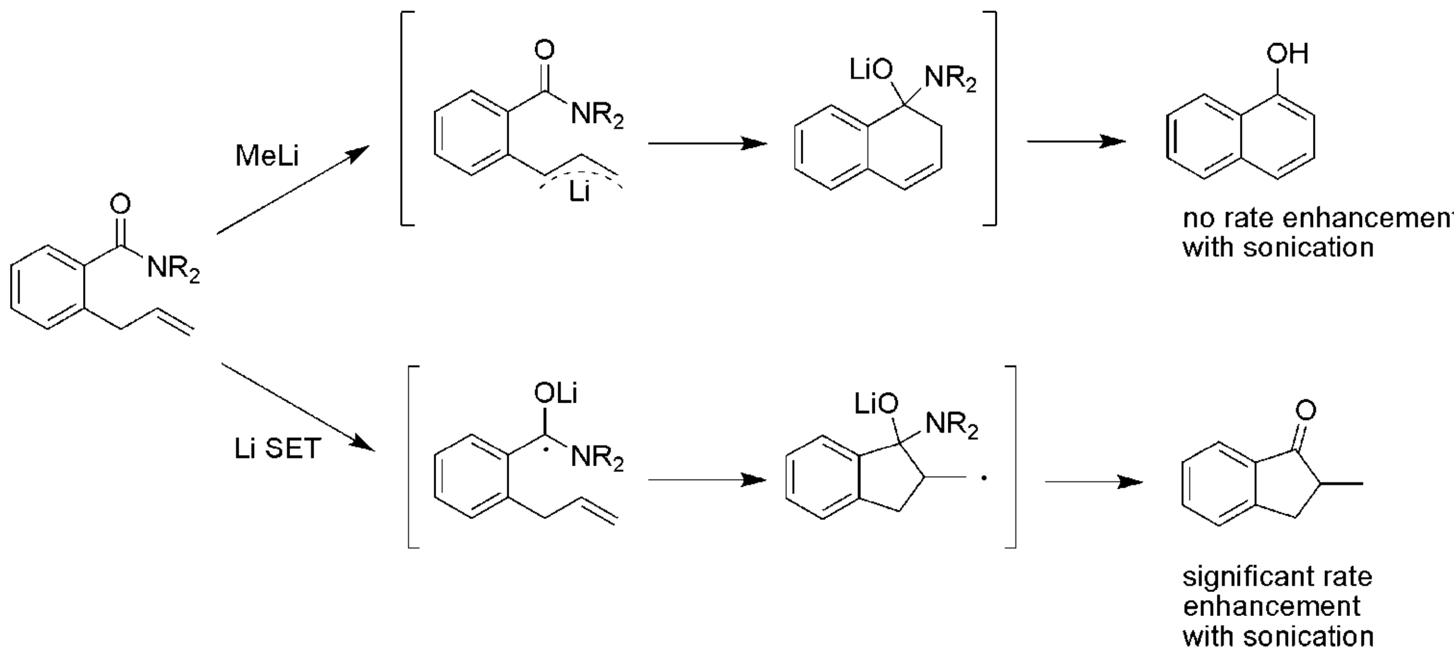
Luche scores again!

Tet. Lett. 29, 4129

Switching, again



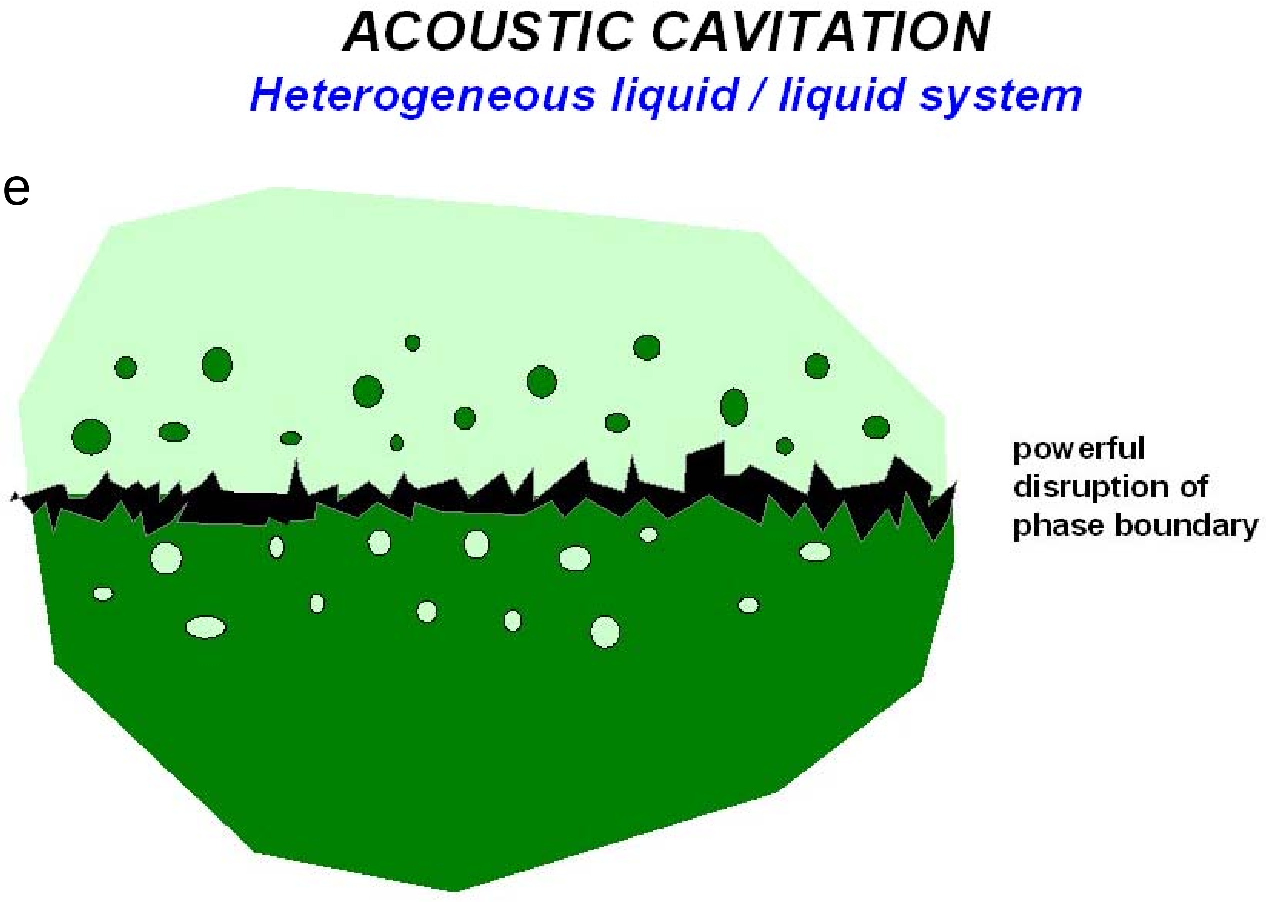
Coll. Czech. Chem. Comm 47, 1334: Tet. Lett. 31, 4125



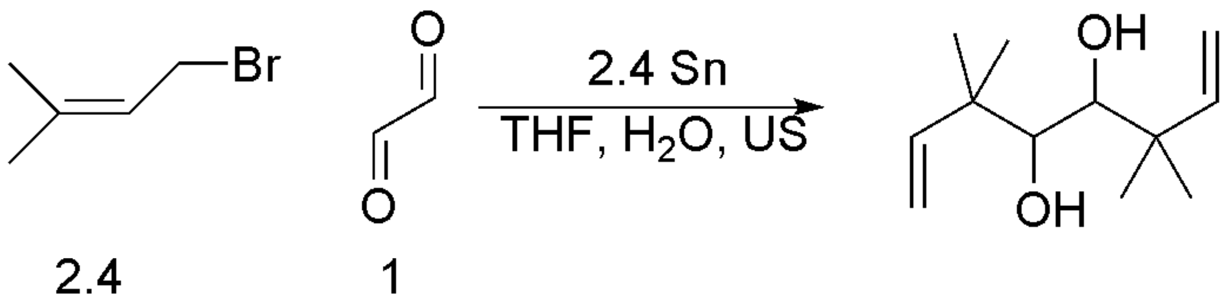
Tet. Lett. 29, 2183; JOC, 51, 271; JOC51, 271

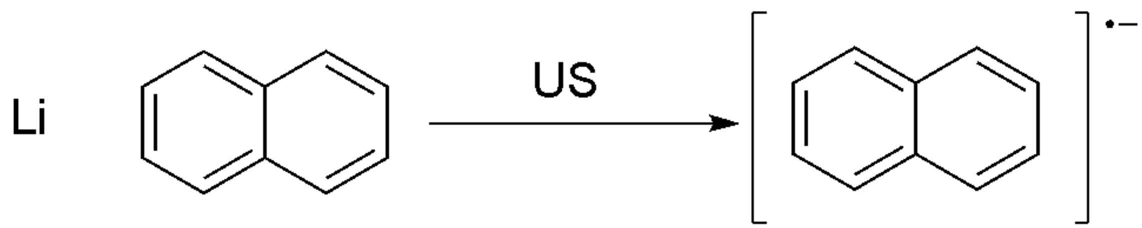
How were the sugars sped up?

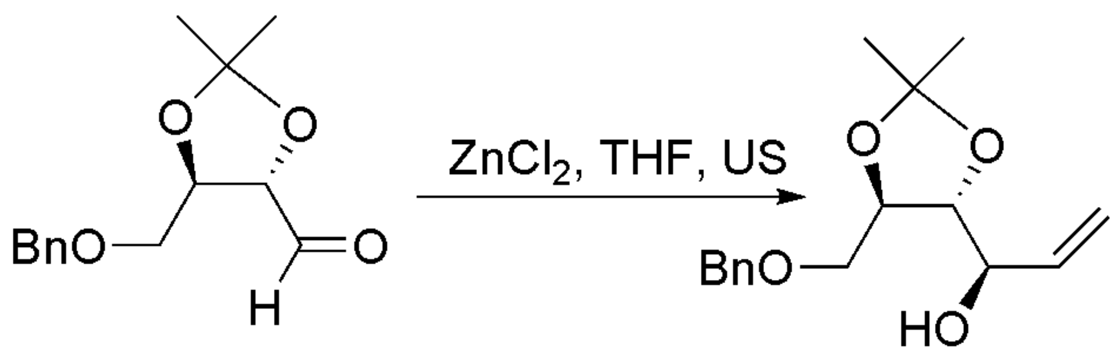
Luche argued carbohydrate chemistry enhanced with US purely due to increased phase mixing



In our group

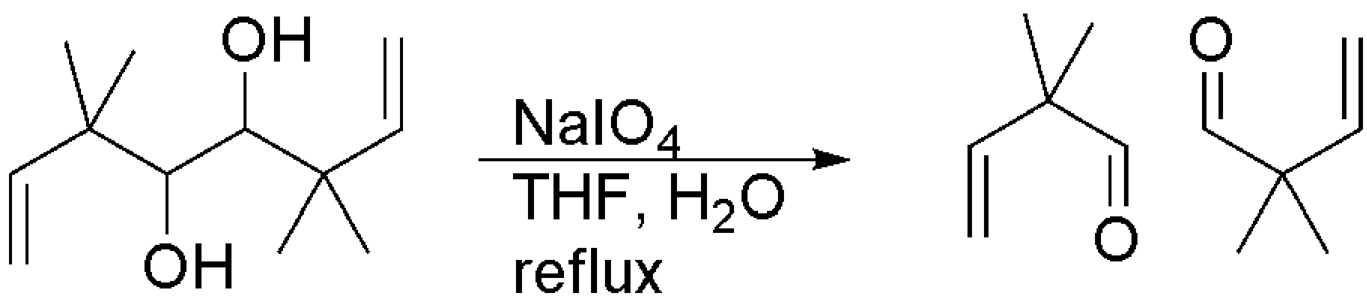






Luke, Timmy

Results from our lab



effects of ultrasound?

Me, today in lab

Take home messages

- US accelerates reactions due to cavitation
- Can be due to mechanical effects
- Can also be due to promotion of SET

Further reading

- How they determined the temperature: JACS 126, 13890; Science 247, 1067; Science 253, 1397; JACS 105, 5781; JACS 105, 6042; JACS 106, 6856
- Bubble dynamics: Am. J. Phys. 68, 211
- Review on high energy sonication: High Energy Chemistry 38, 135
- HWE via sonochemistry: JOC 52, 3875; JACS 104, 3987

Special thanks to Dee and Mark