Advanced Organic Chemistry/ Organic Synthesis – CH 621

Ultrasound Assisted Organic Synthesis (Sonochemistry)

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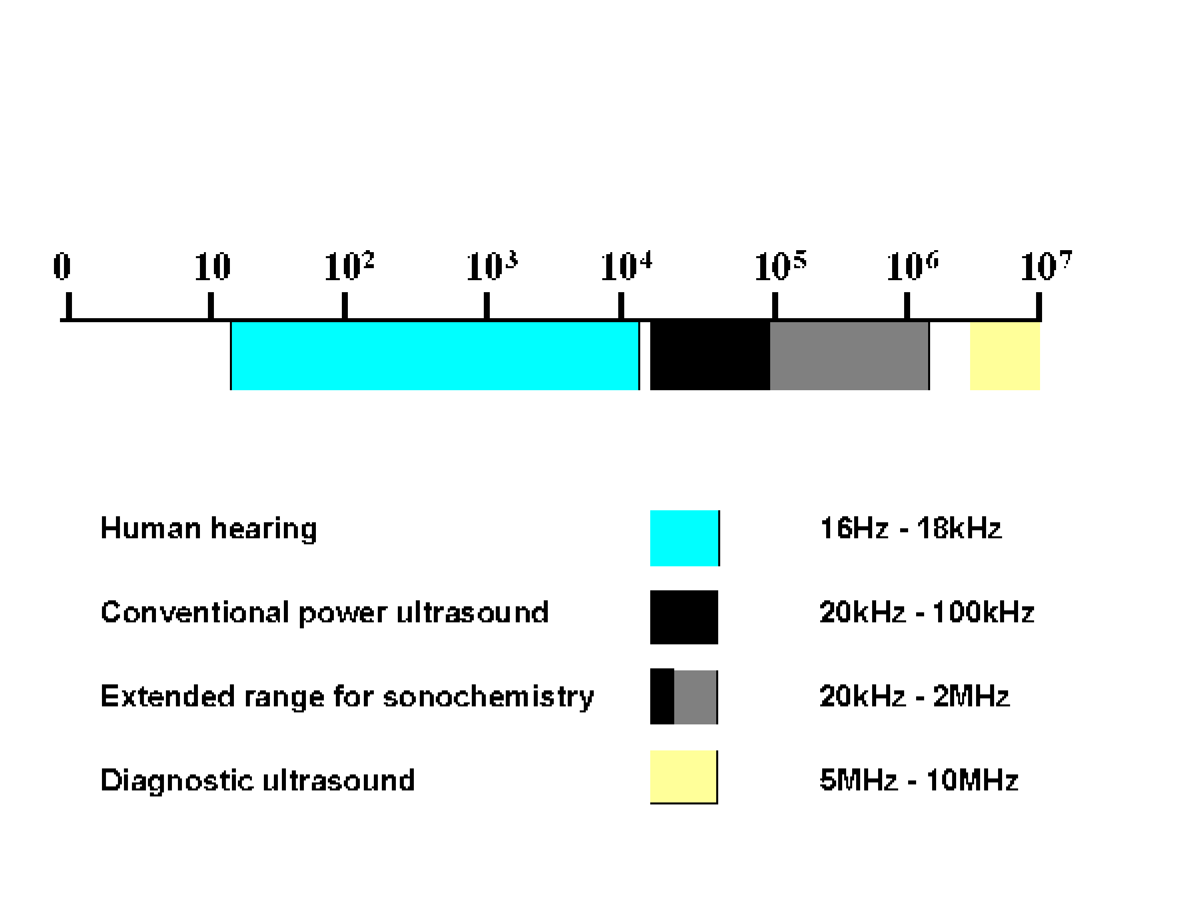
Ultrasonics/Sonochemistry - Historical Overwiev

Ultrasonics

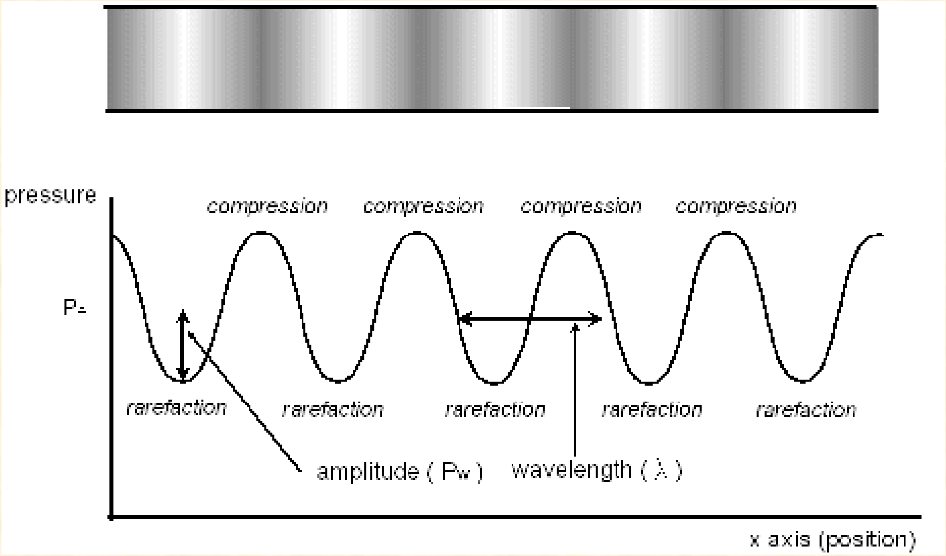
- Ultrasounds (20-10 000 kHz)
- 1880 Piezoelectricity (Curie brothers)
- 1893 Galton
- 1912 TITANIC
- 1912 Behm (Echo technique)
- 1917 Langevin (Ultrasonic variation, Icebergs, Submarines)
- 1945 Application in chemistry

Ultrasonics/Sonochemistry – Basics



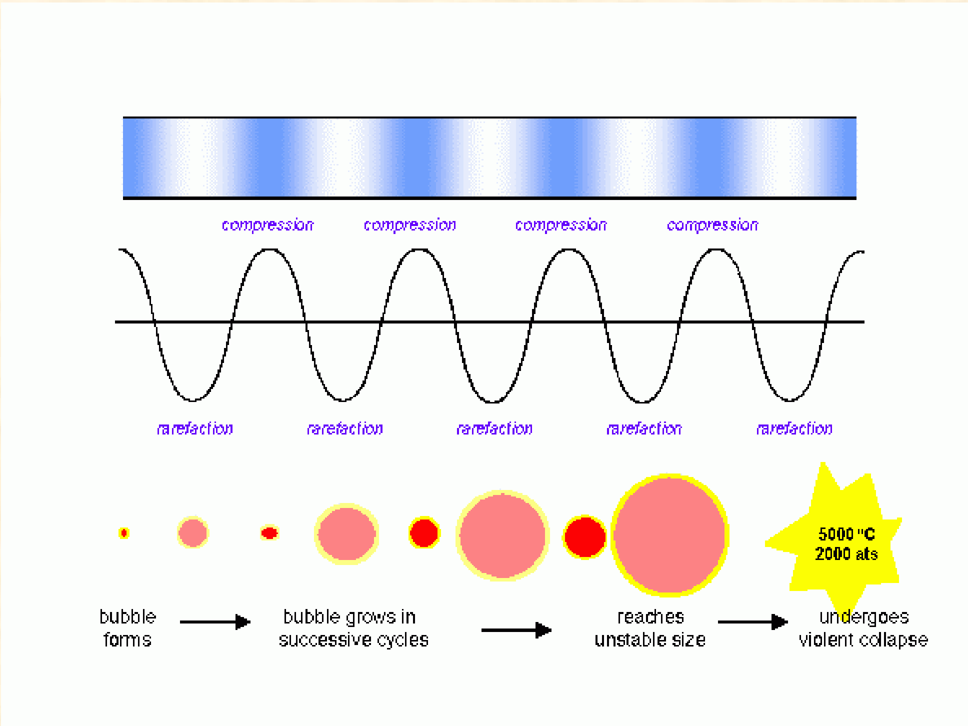
Frequency ranges of sound

Ultrasonics/Sonochemistry – Basics

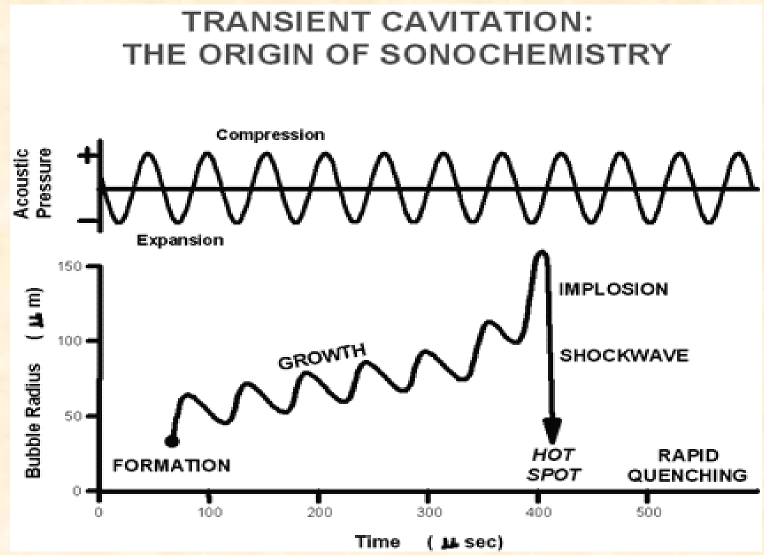


Sound transmission through a medium

Ultrasonics/Sonochemistry – Acoustic Cavitation



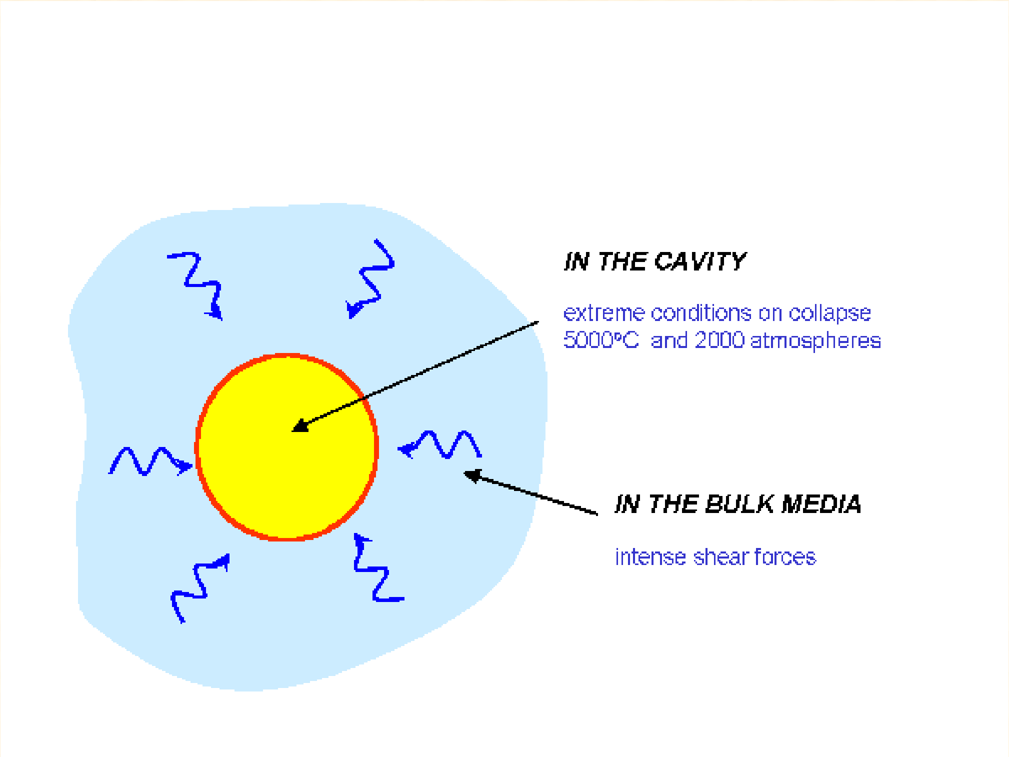
Formation of an acoustic bubble



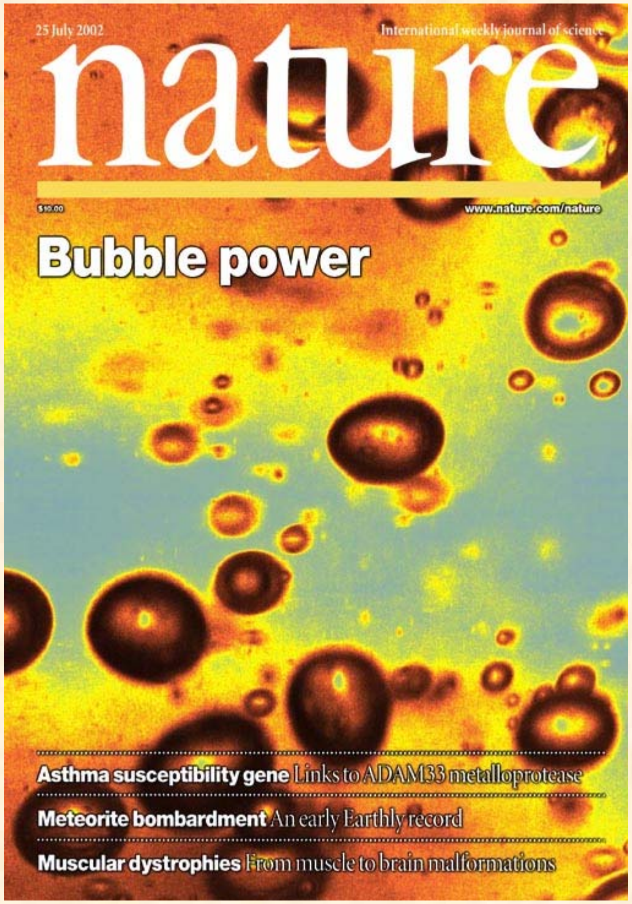
Bubble size and cavitation dynamics

Transient cavitation

Ultrasonics/Sonochemistry – Acoustic Cavitation

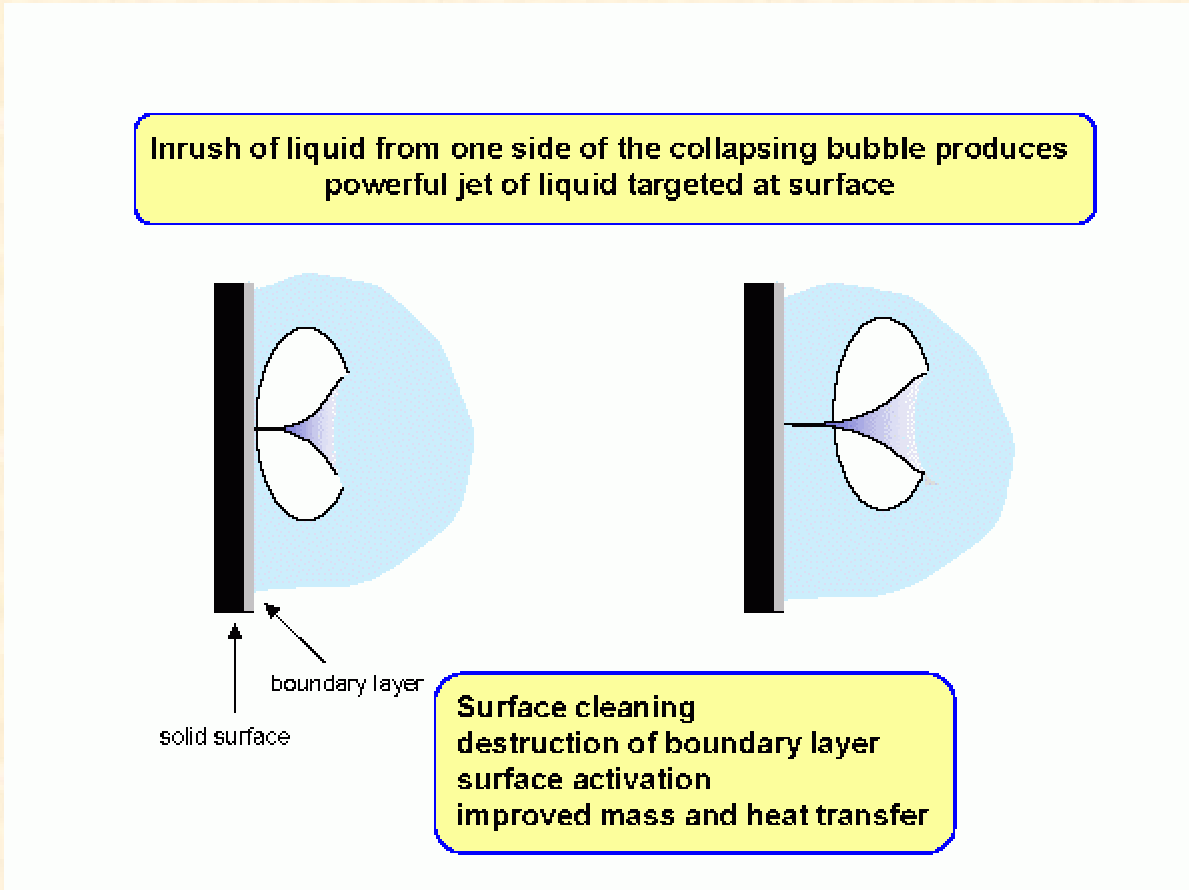


Acoustic cavitation in a homogeneous liquid



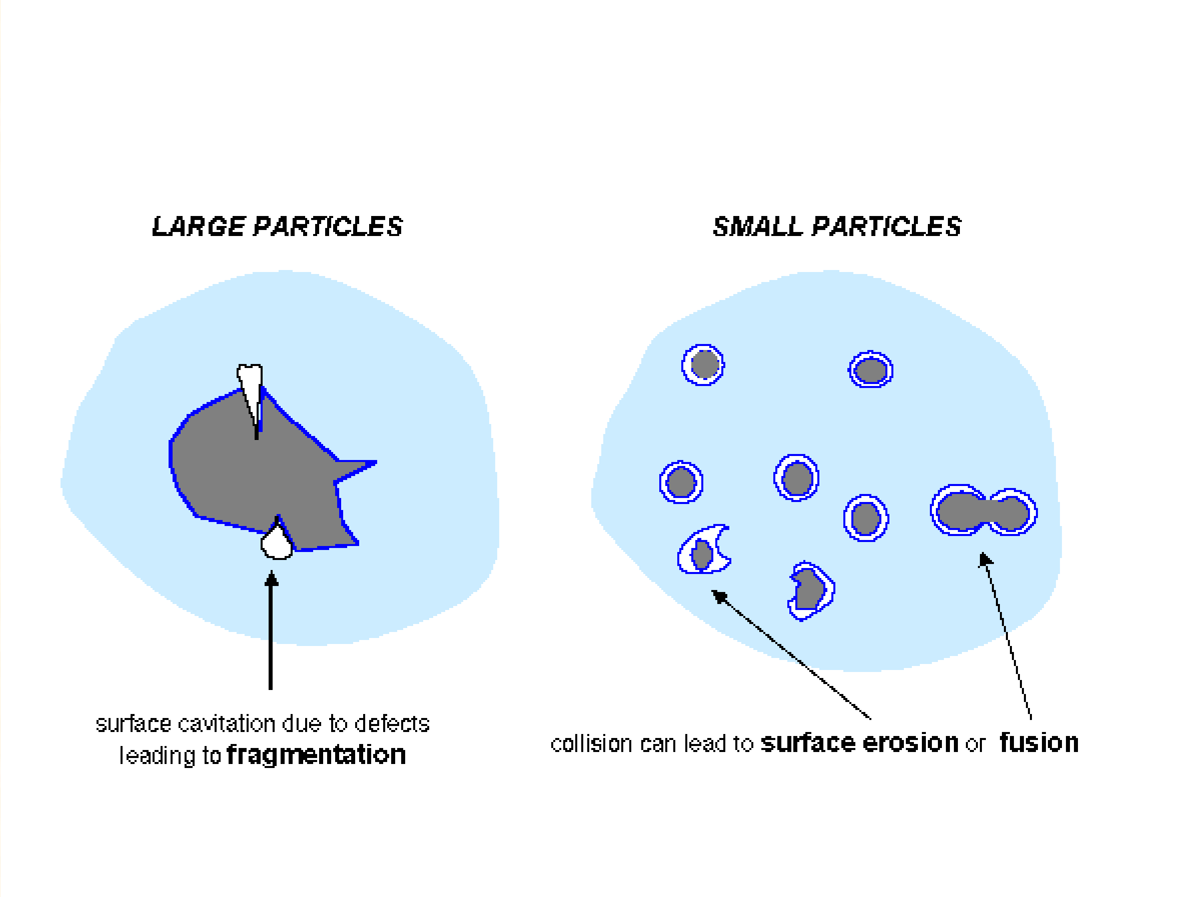
Suslick - ~ 4-5000 K

Ultrasonics/Sonochemistry – Acoustic Cavitation



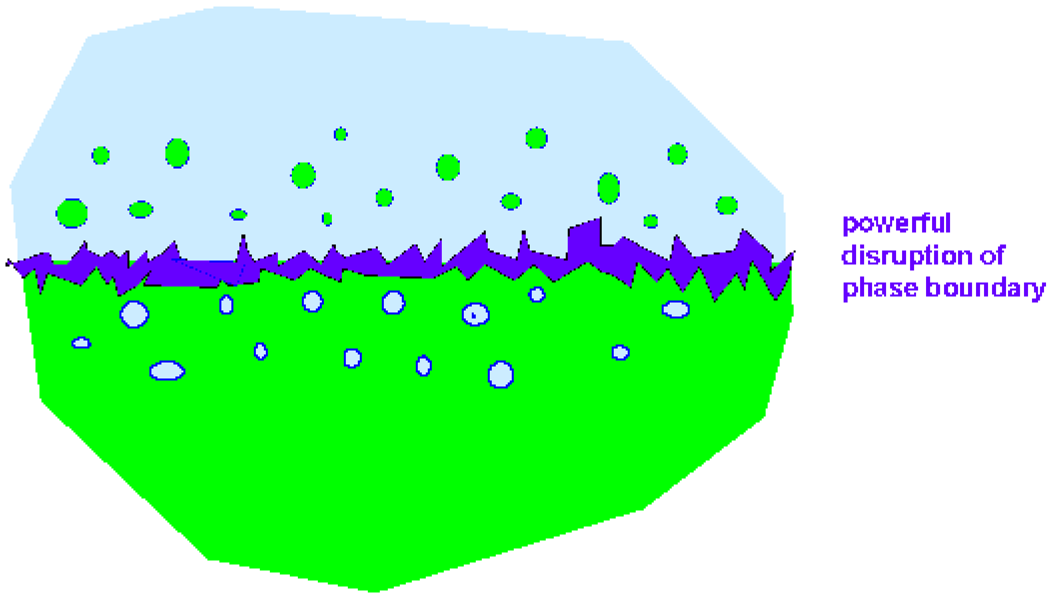
Acoustic cavitation in solid/liquid system

Ultrasonics/Sonochemistry – Acoustic Cavitation



Acoustic cavitation in solid/liquid system

Ultrasonics/Sonochemistry – Acoustic Cavitation



Acoustic cavitation in liquid/liquid system

Ultrasonics/Sonochemistry – Sonochemical Effect

Specific ultrasonic effect ? Yes and No

No - another internal heating approach

Yes - The temperature dependence of E_A of different reactions could be significantly different – change in selectivities

- Very effective mixing
- Cavitation
- Surface cleaning

Ultrasonics/Sonochemistry – Experimental Parameters

1. Acoustic frequency

Increasing frequency – increasing energy

Theory - usually higher reaction rate

Real life – optimum frequency as we have to balance reactivity/selectivity

The effect is different for every reaction and general rule can not be made.

Ultrasonics/Sonochemistry – Sonochemical Effect

2. Acoustic power

Similar as frequency, however, the extent of increase is limited

Optimum

Ultrasonics/Sonochemistry – Sonochemical Effect

3. Temperature

Cavitation bubbles – energy of collapse

Pressure inside the bubble

In general lower temperature is better, but again there is an optimum

as higher temperature increases the probability of the cavitation

Ultrasonics/Sonochemistry – Sonochemical Effect

4. External (static) pressure

Not quite clear, but in general higher pressure is better.

Role of particles (ultrafiltration)

Ultrasonics/Sonochemistry – Sonochemical Effect

5. Gas

Polytrop ratio ($\gamma = C_p/C_v$), thermal conductivity, and solubility

Usually inert gases are the best (noble gases)

6. Solvent

Should be as inert as possible, and stable toward ultrasounds

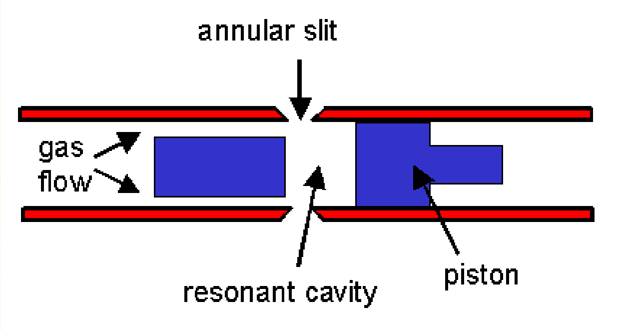
Sonolysis of the solvent

Usually high bioling point is preferred, but it is controversial as diethylether is a good solvent in many applications.

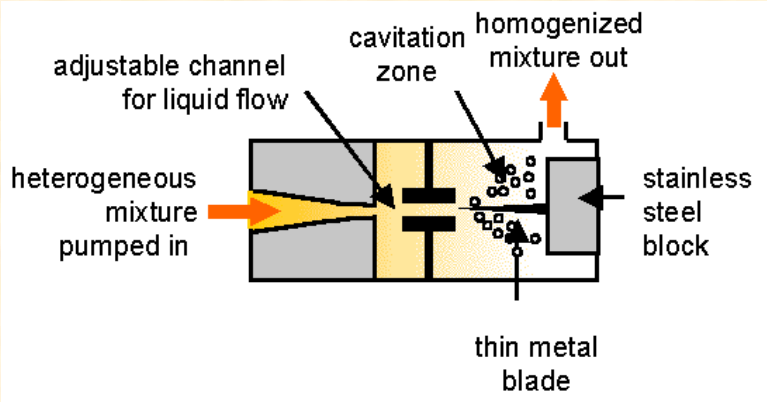
Ultrasonics/Sonochemistry – Experimental Parameters

Experimental parameter	Physical parameter	Effect
Acoustic frequency	Period of bubble collapse	Change in the size of the bubbles
Acoustic power	Size of the reaction zone	The number of cavitation phenomena in a unit volume
Temperature	Vapor pressure of liquid Themal activation	The content of bubbles, the intensity of collapse Secondary reactions
Static pressure	Total pressure Solubility of gas	Intesity of collapse The content of bubbles
Gas	Politrop ratio Thermal conductivity Chemical reactivity solubility	Intesity of collapse Primer and secondary reactions The content of bubbles
Solvent	Vapor pressure Surface tension Viscosity Chemical reactivity	Intesity of collapse Limit of transient cavitation Primer and secondary reactions

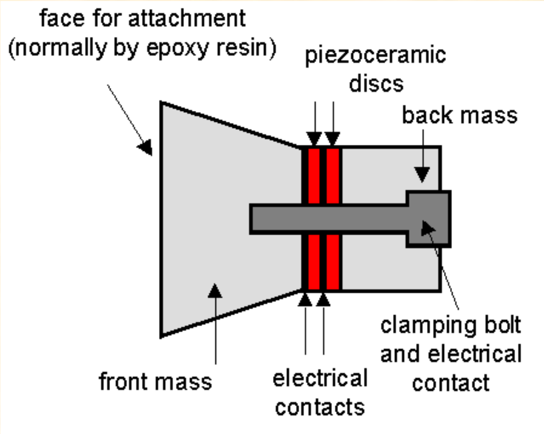
Ultrasonics/Sonochemistry – Transducers



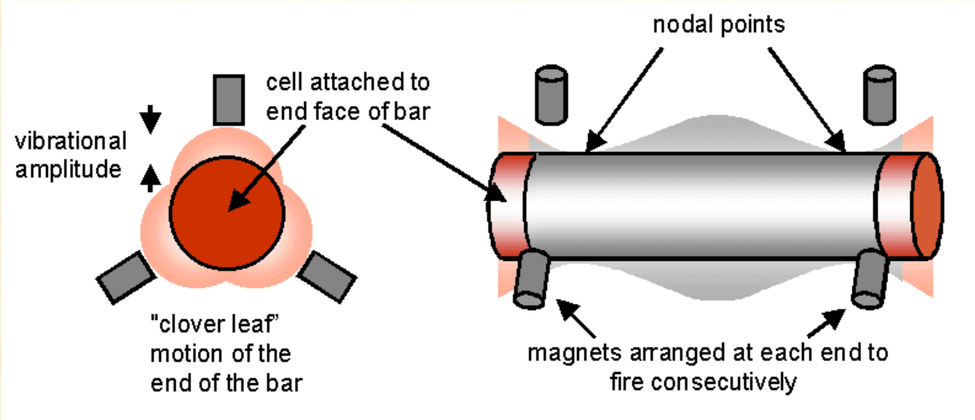
Galton whistle (physical)



Liquid whistle (physical)

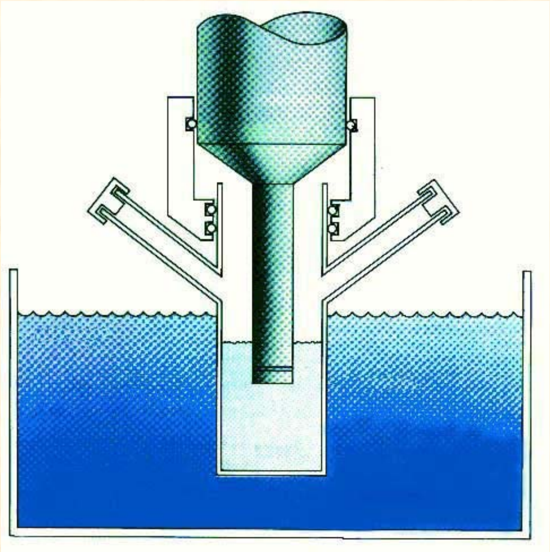


Piezoelectric sandwich transcducer



Magnetostrictive transcducer

Ultrasonics/Sonochemistry – Reactors



Ultrasonics/Sonochemistry – Applications

- Electronics industry (coating with metals)
- Therapy (surgery with ultrasounds), diagnostics
- Food industry
- Materials (metallurgy)
- Synthesis
- Environmental applications

Ultrasonics/Sonochemistry – Synthesis

Applications in Organic Synthesis

1. Homogeneous Sonochemistry
- Aqueous medium
- Non-aqueous media

2. Heterogeneous Sonochemitsry
- Phase Transfer Catalysis
- Reactions with metals
- Heterogeneous Catalysis

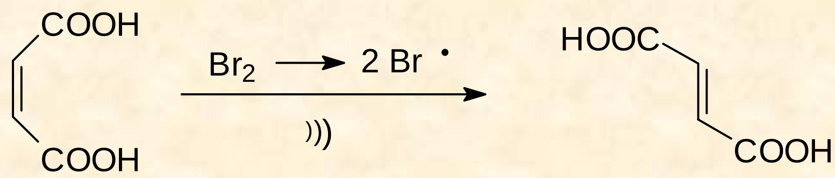
3. Enzyme reactions

Ultrasonics/Sonochemistry – Synthesis

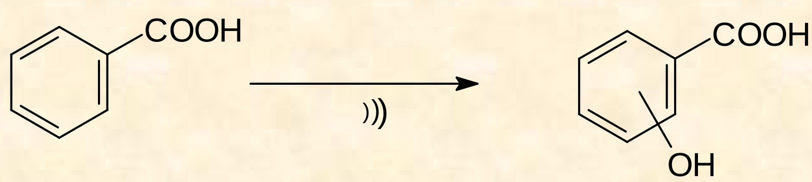
1. Homogeneous sonochemistry

1.1. Aqueous sonochemistry

$$H_2O \longrightarrow H^\bullet + OH^\bullet$$
$$H^\bullet + OH^\bullet \longrightarrow H_2O$$
$$2\,H\bullet \longrightarrow H_2$$
$$2\,OH\bullet \longrightarrow H_2O_2$$
$$2\,OH\bullet \longrightarrow O^\bullet + H_2O$$
$$2\,O\bullet \longrightarrow O_2$$
$$0{,}5\,O_2 + 2\,H\bullet \longrightarrow H_2O$$



(2.8)



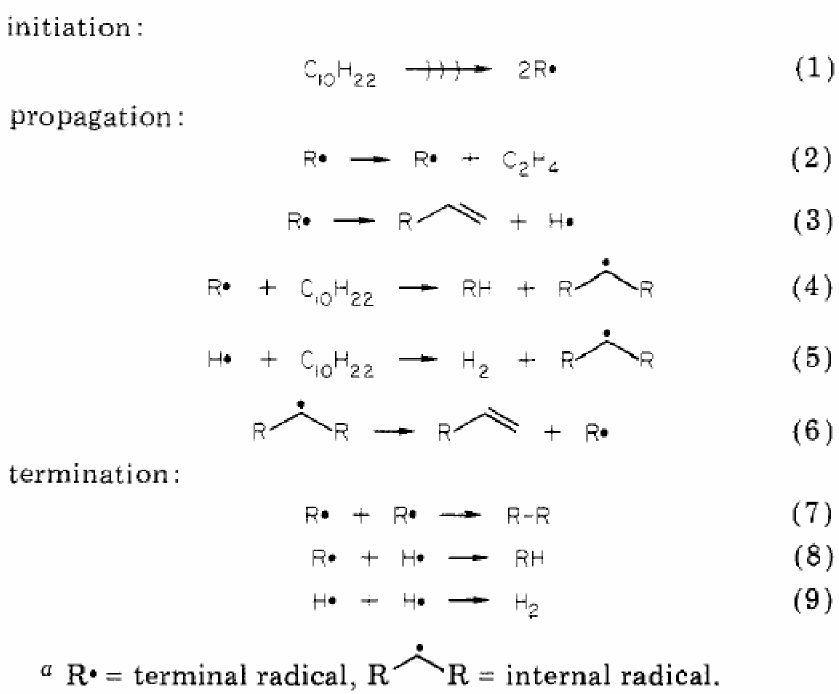
(2.9)

Ultrasonics/Sonochemistry – Synthesis

1. Homogeneous sonochemistry

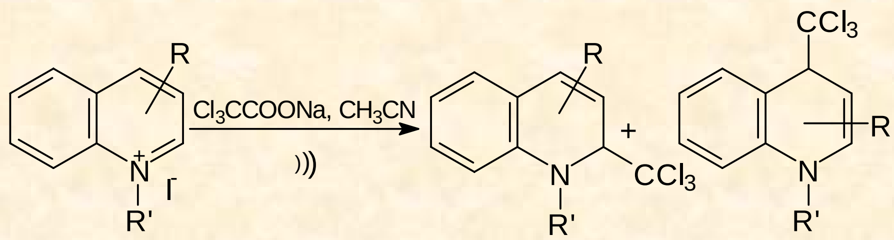
1.2. Non-Aqueous sonochemistry

Scheme I: Rice Radical Chain Mechanism[a]



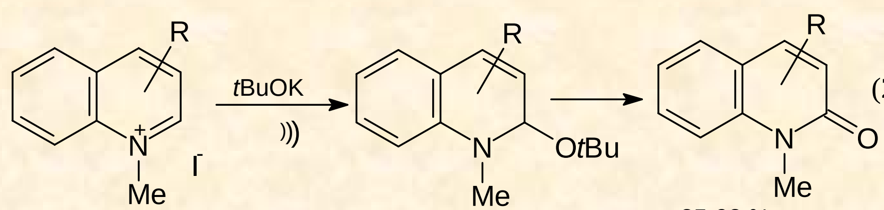
Ultrasonics/Sonochemistry – Synthesis

1.2. Non-Aqueous sonochemistry



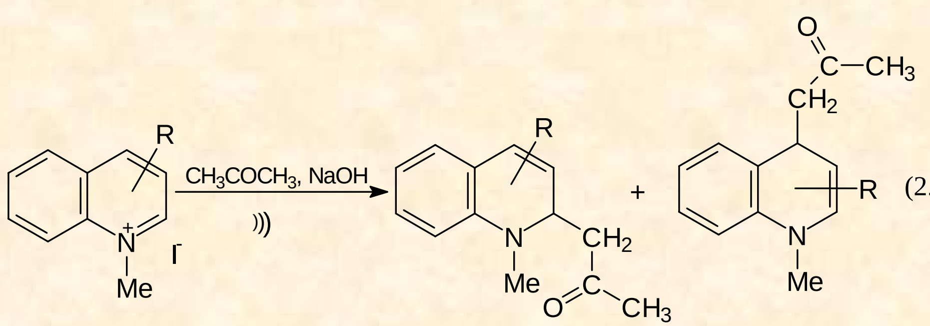
(2.14)

70-100 %



(2.15)

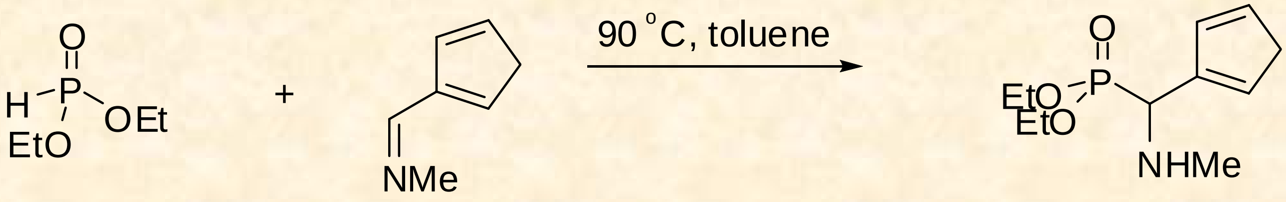
85-98 %



(2.16)

91 - 98 %

1.2. Non-Aqueous sonochemistry

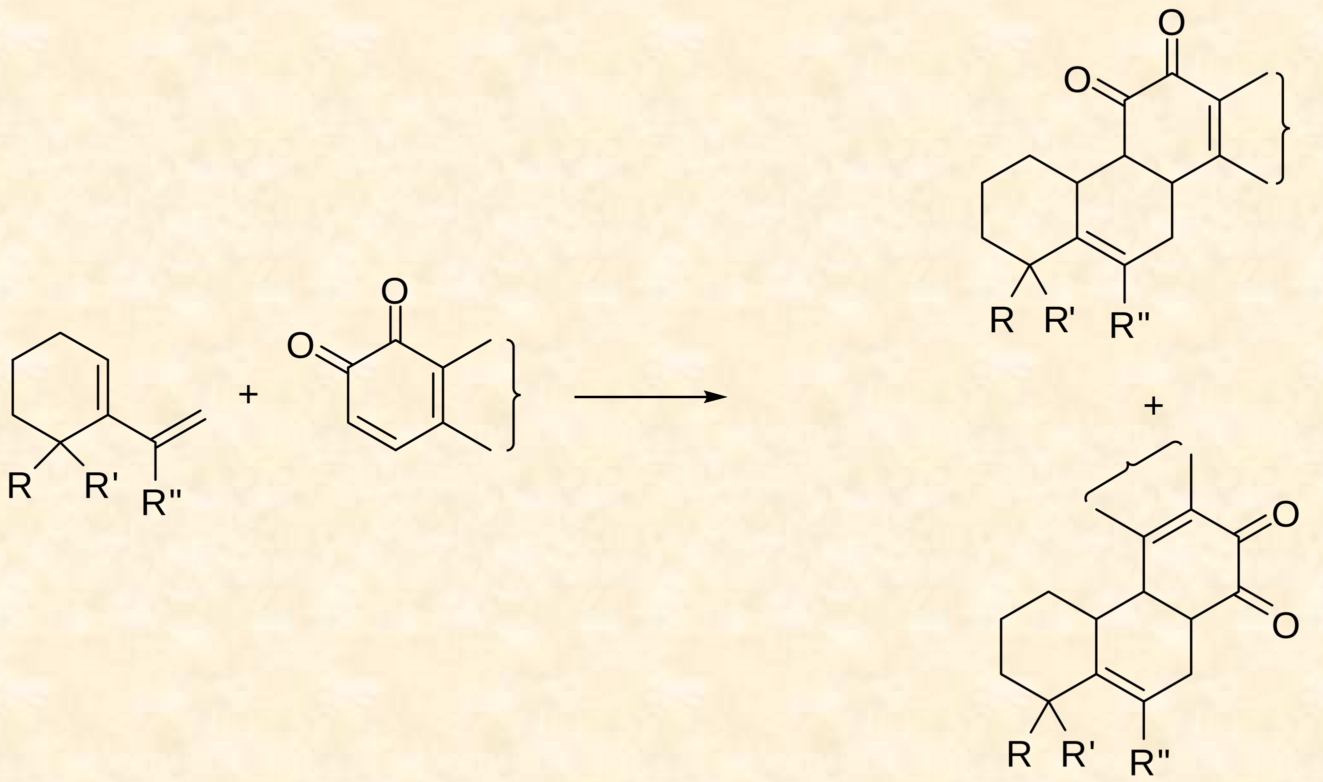


Yield (%)

	15 min	30 min	60 min	120 min
stirring	0	0	<5	37
sonication	12	32	67	82

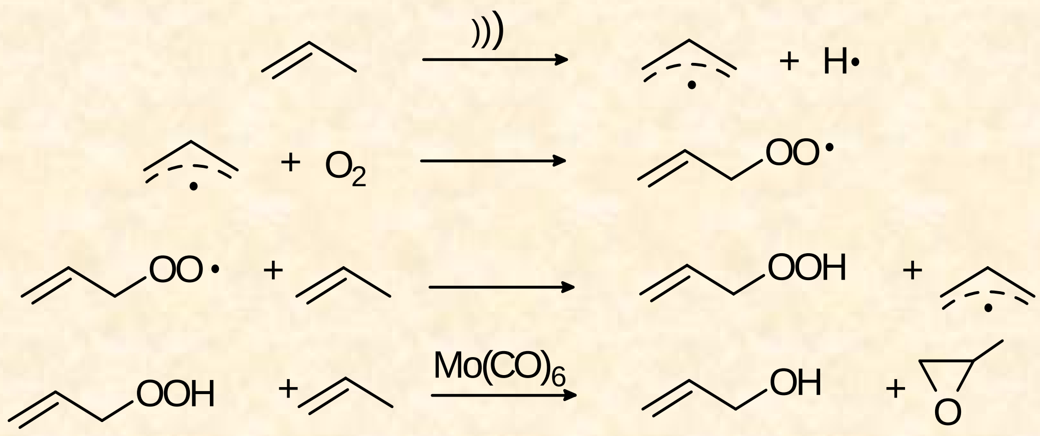
Ultrasonics/Sonochemistry – Synthesis

1.2. Non-Aqueous sonochemistry



	Yield (%)
stirring	10-53
sonication	57-93

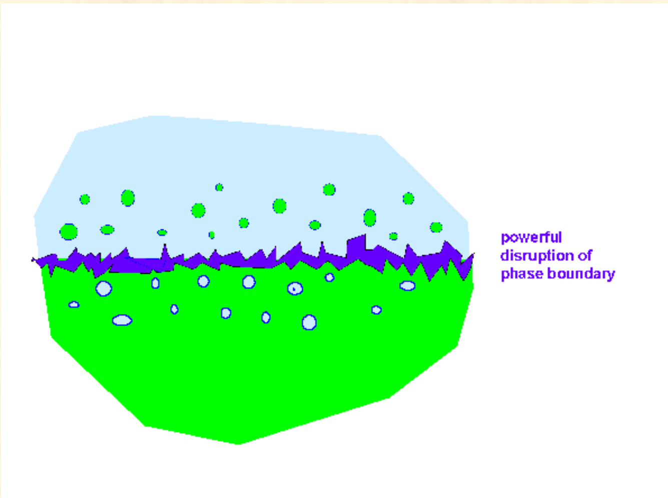
1.2. Non-Aqueous sonochemistry

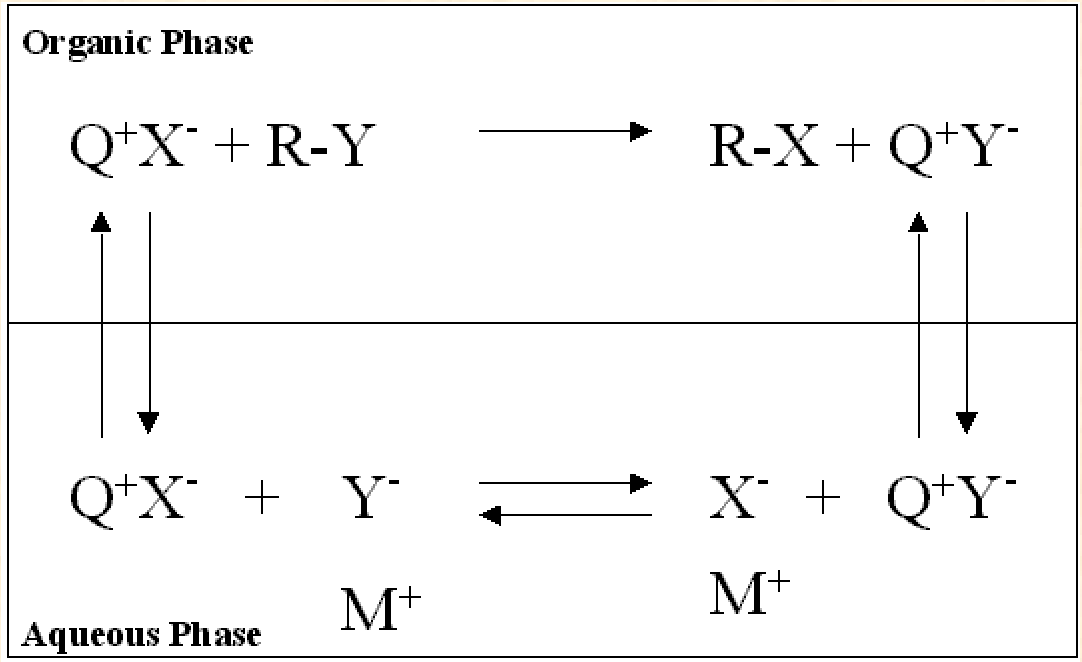


Ultrasonics/Sonochemistry – Synthesis

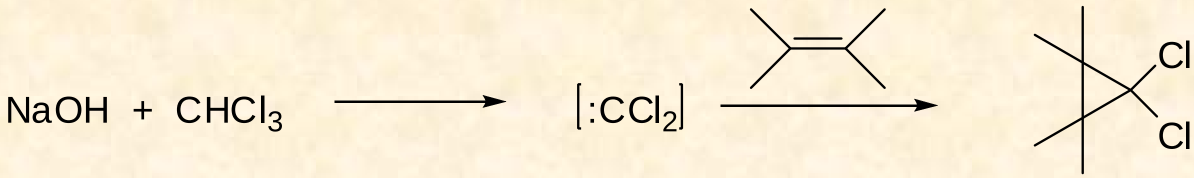
2. Heterogeneous sonochemistry

2.1. Phase transfer catalysis

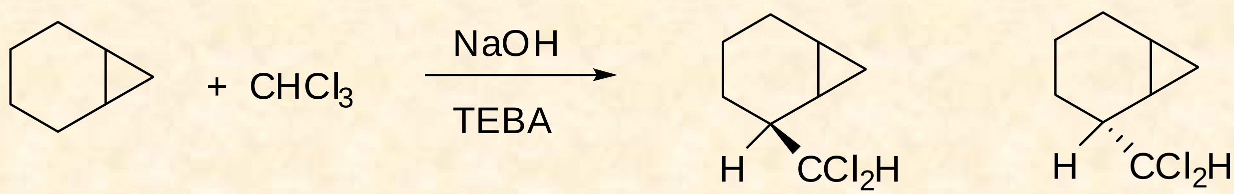




2.1. Phase transfer catalysis



0.7-5h 74-99%

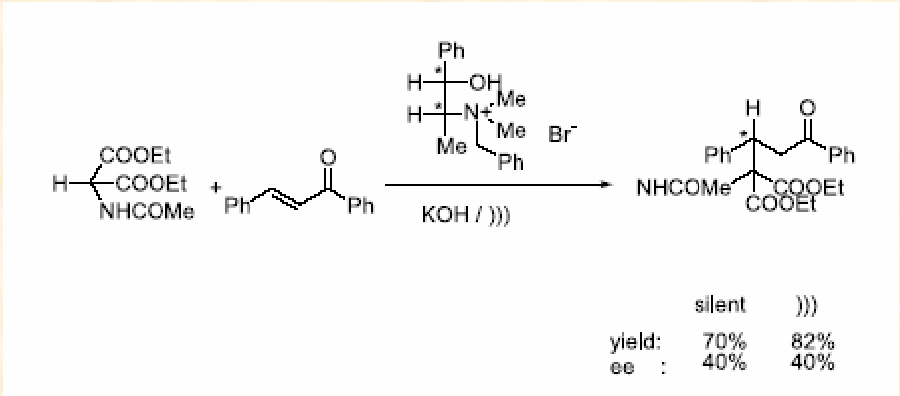


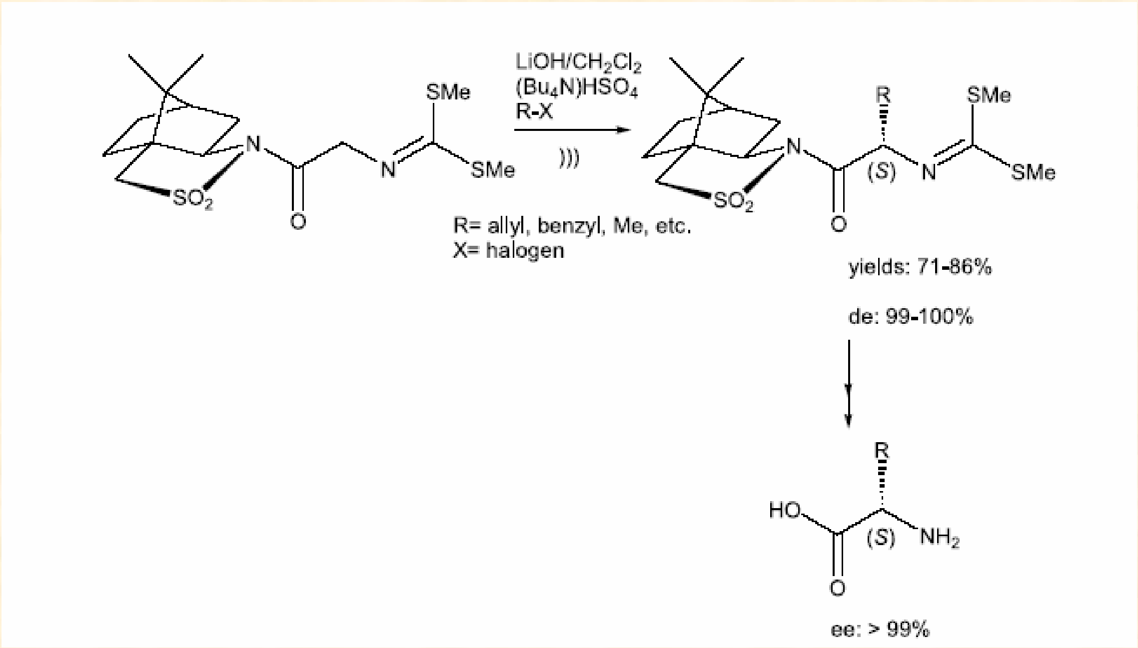
4.3 1

stirring 9 h 15%
sonication, 3h 83%

Ultrasonics/Sonochemistry – Synthesis

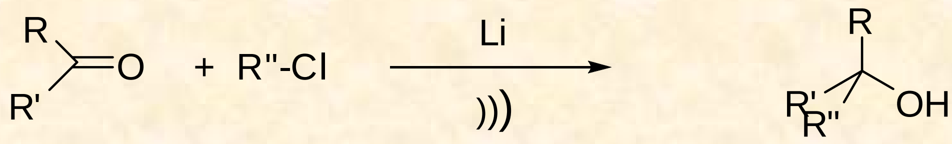
2.1. Phase transfer catalysis



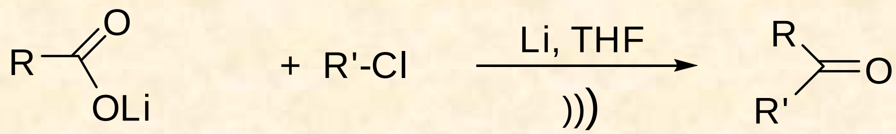


Ultrasonics/Sonochemistry – Synthesis

2.2. Reactions with metals

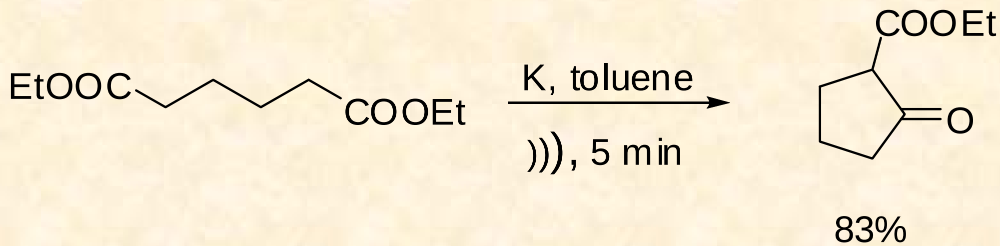


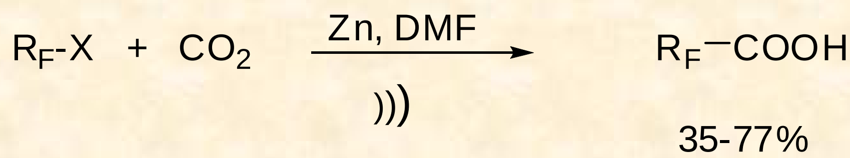
10-40 min   68-99%

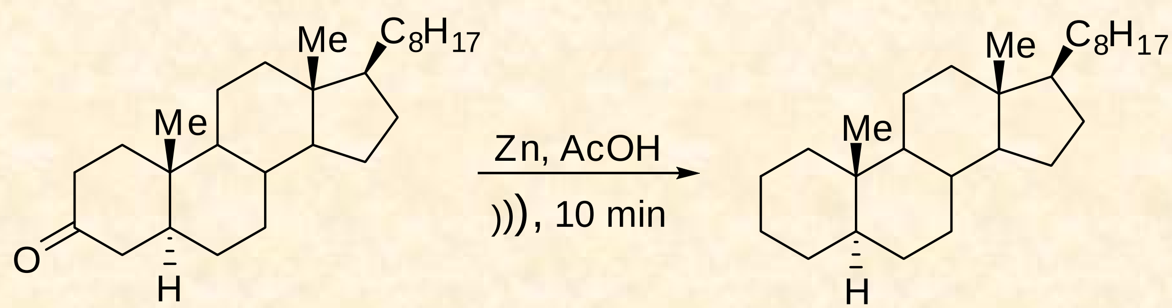


72-99%

2.2. Reactions with metals

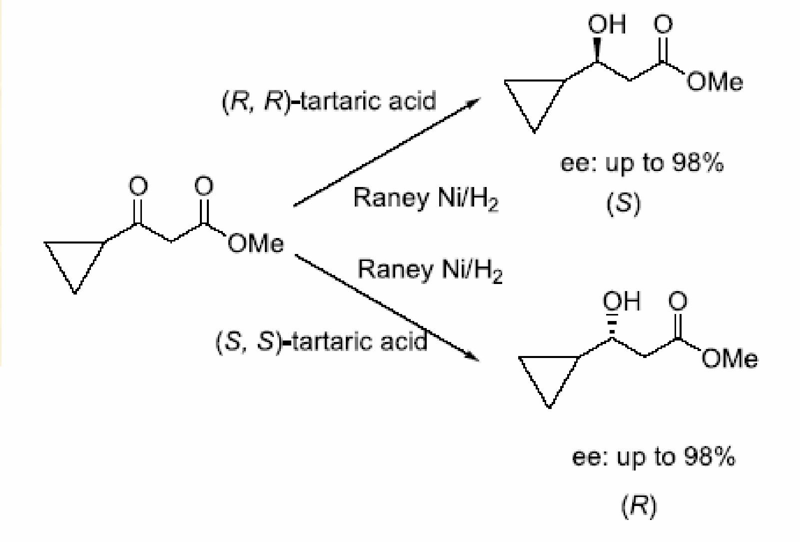


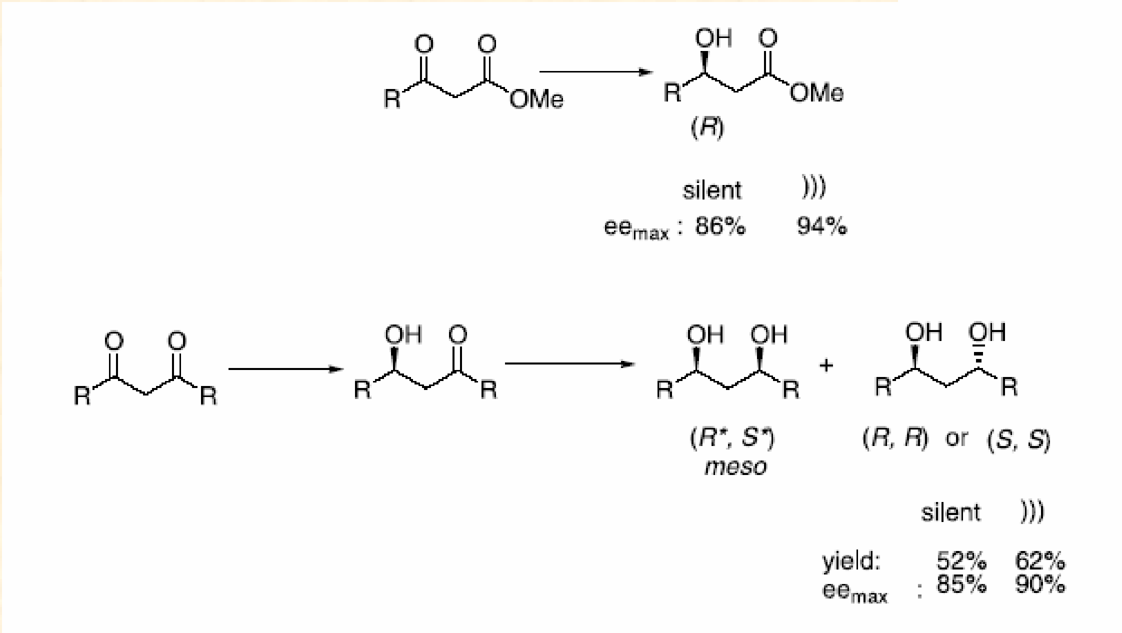




Ultrasonics/Sonochemistry – Synthesis

2.3. Heterogeneous catalysis

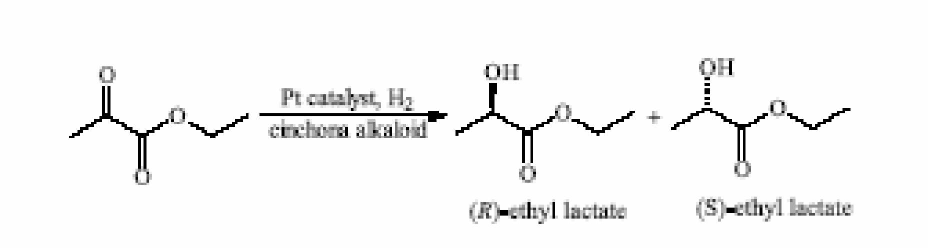




Catalytic system: Raney Ni (presonicated)
(*R*, *R*)-tartaric acid-NaBr

Ultrasonics/Sonochemistry – Synthesis

2.3. Heterogeneous catalysis



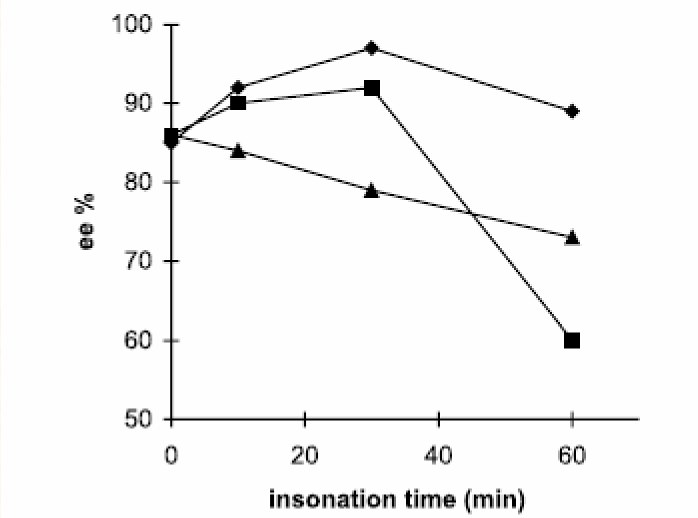


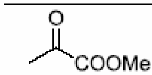
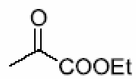
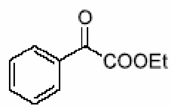
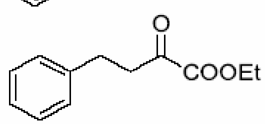
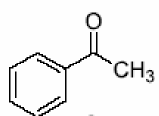
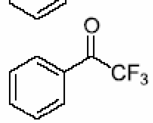
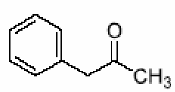
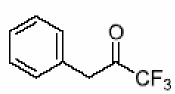
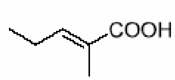
Fig. 1. Effect of ultrasound frequency on the optical yield sonochemical hydrogenation of ethyl pyruvate over cinchonidine modified Pt/Al_2O_3 catalyst (◆ – 20 kHz, ■ – 35 kHz, ▲ – 47 kHz). The ee values were determined at 100% conversion.

Ultrasonics/Sonochemistry – Synthesis

2.3. Heterogeneous catalysis

Table 4

Sonochemical and silent enantioselective hydrogenation of activated ketones, ketoesters and unsaturated carboxylic acids over 5% Pt/Al_2O_3 (C=O double bond) and 5% Pd/Al_2O_3 (C=C double bond) using different cinchona modifiers under hydrogen pressure

Substrate	Modifier	Catalyst	Hydrogen pressure (bar)	Solvent	Major product	Optical yield (ee%)	
						⤸	)))
	CD	E4759	10	AcOH	*R*	94	95
	CD	E40655	10	AcOH	*R*	85	97
	MeOHCD	E40655	10	AcOH	*R*	78	98
	CD	E4759	10	AcOH	*R*	88	92
	CD CN	E4759 E4759	10 10	AcOH AcOH	*R* *S*	79 85	96 92
	CD	E4759	10	DCB	R	6	8
	CD	E4759	10	DCB	*R*	46	49
	CD	E4759	10	DCB	*R*	7	8
	CD	E4759	10	DCB	*R*	18	18
	CD	E40692	50	Toluene	*S*	50	62

DCB – 1,2-dichlorobenzene.

Microwaves/Sonochemistry – References

- http://www.shiga-med.ac.jp/chemistry/sonochemRes.html
- Luche, J. L., Synthetic Organic Sonochemistry, Plenum Press, 2001
- Suslick, K. S., Ultrasound: Its Chemical, Physical, and Biological Effects; VCH, 1988.
- Mason, T. J., Sonochemistry: Current Uses and Future Prospect in Chemical and Industrial Processing, RSC, 1999