

# Green Synthesis 5

# Unusual Forms of Energy in Synthesis

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# Microwave Irradiation – Historical Overview

## Microwave Chemistry

- microwaves (2.45 GHz)
- WWII – radar (magnetron)
- 1950s food industry
- 1984 first application in chemical synthesis

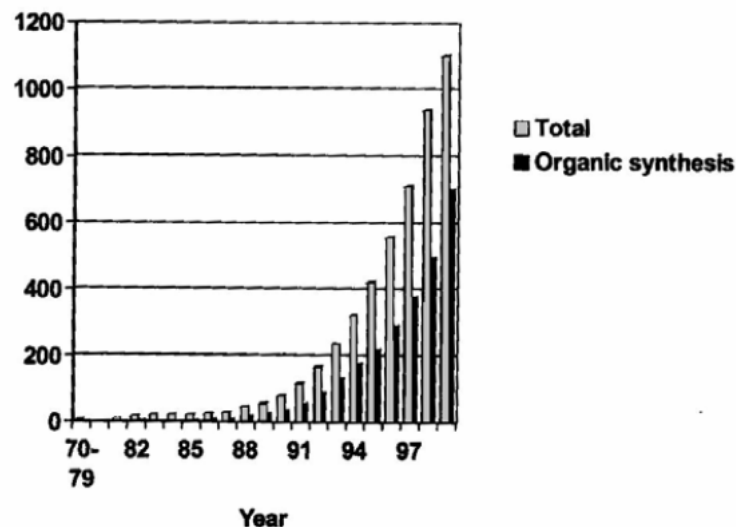
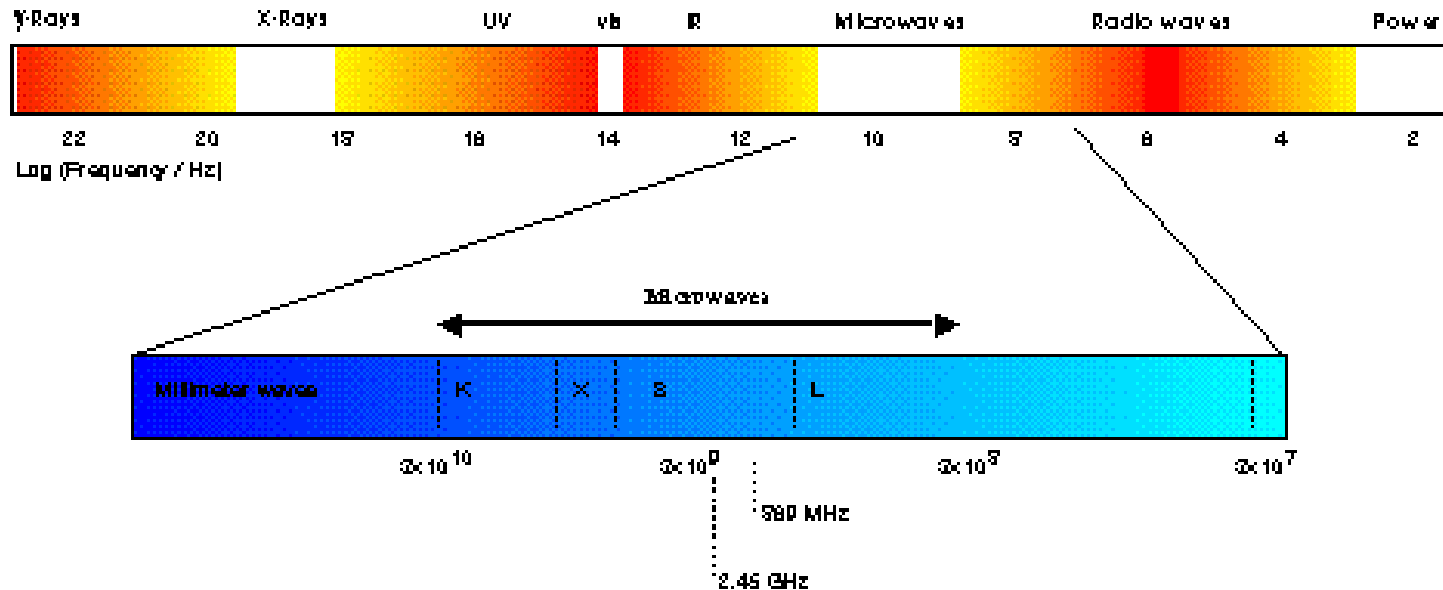


Fig. 1 Published articles involving microwave irradiation since 1970<sup>41</sup>

# Microwave Irradiation –



The electromagnetic spectrum

# Microwave Irradiation – Heating Effect



## Dielectric polarization

$\alpha_t$  – total polarization

$\alpha_e$  - electron polarization

$\alpha_a$  - atom polarization

$\alpha_i$  - interfacial polarisation  
(Maxwell – Wagner effect)

$\alpha_d$  – dipolar polarization

$$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i$$

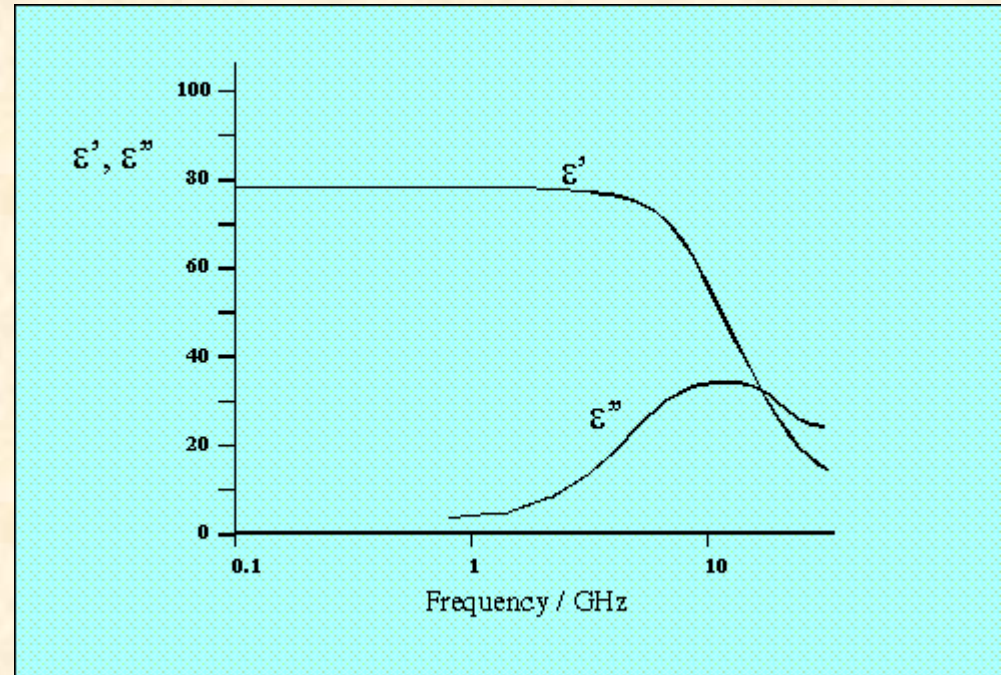
# Microwave Irradiation – Heating Effect

Dipolar polarization

$$\tan \delta = \varepsilon'' / \varepsilon'$$

$\varepsilon'$  – dielectric constant

$\varepsilon''$  – dielectric loss



Variation of dielectric properties as a function of frequency

$$D_p \approx \lambda_0 \sqrt{(\varepsilon' / \varepsilon'')}$$

Depth of irradiation

# Microwave Irradiation – Heating Effect

## Interfacial polarization

$$\epsilon''_i \cong \frac{9v\epsilon' f_{\max}}{1,8 \cdot 10^{10} \sigma} \frac{(\omega\tau)}{(1 + \omega^2 \tau^2)}$$

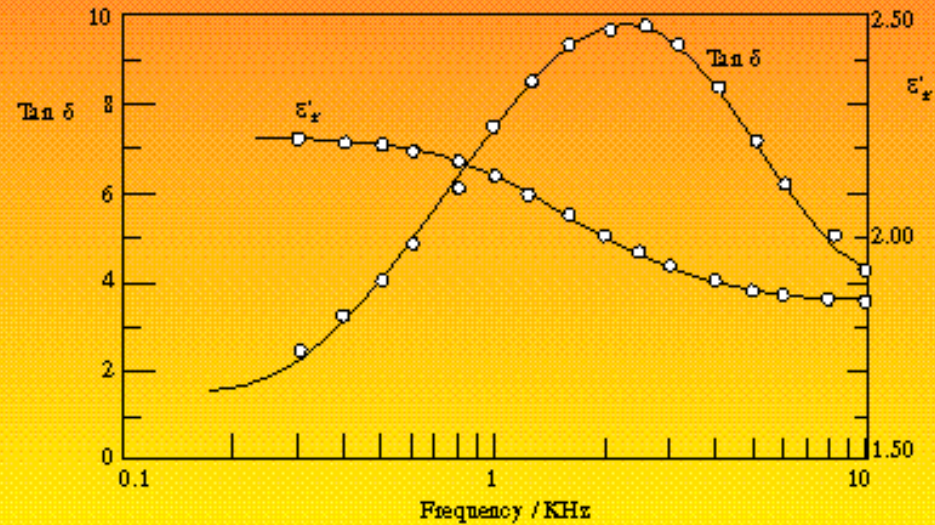
$v$  – volume

$f_{\max}$  – frequency at max loss

$\sigma$  – conductivity

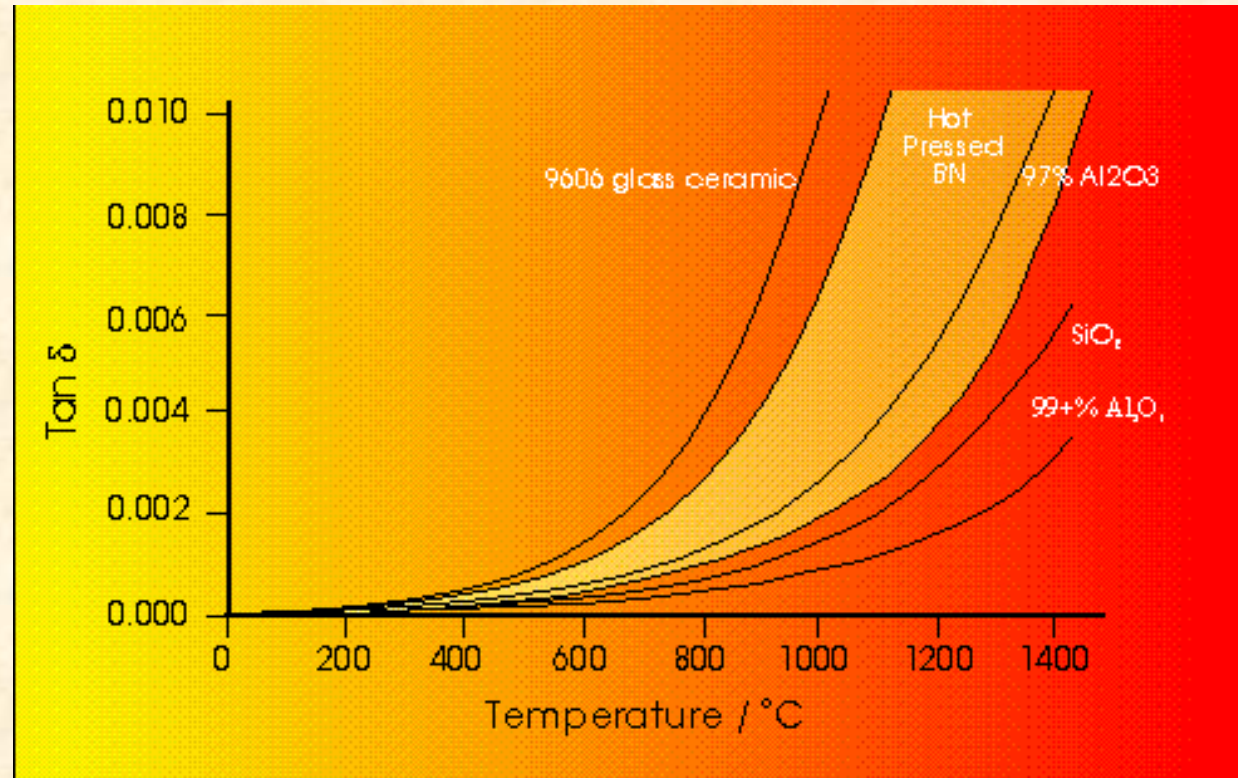
$\omega$  – frequency of relaxation

$\tau$  – time of relaxation



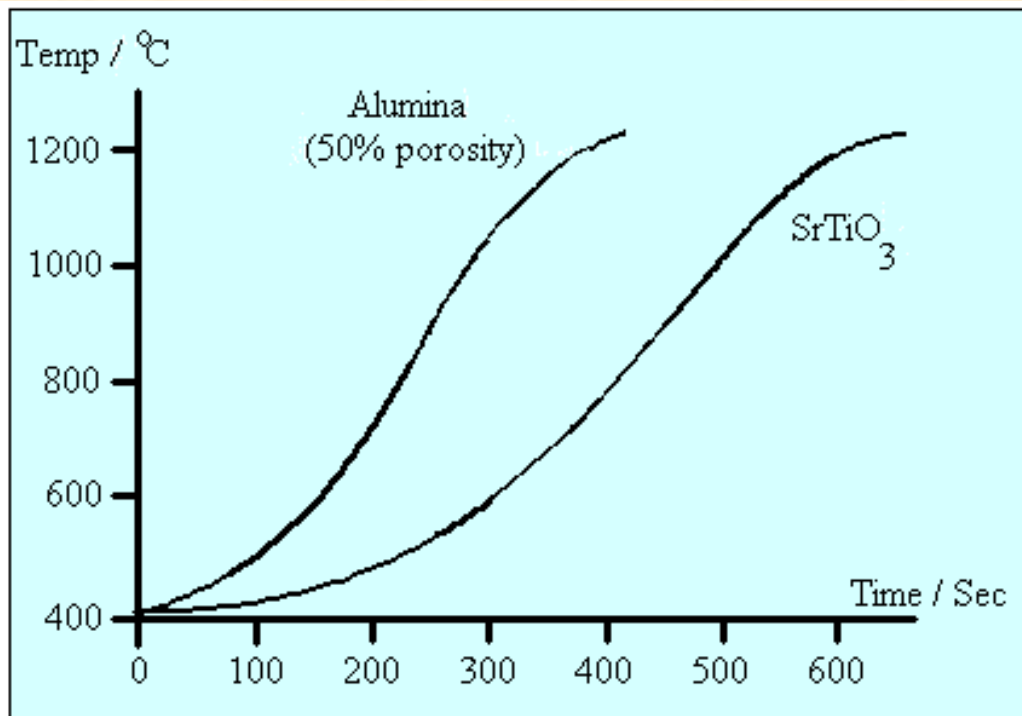
# Microwave Irradiation – Heating Effect

## Interfacial polarization



# Microwave Irradiation – Heating Effect

## Interfacial polarization



# Microwave Irradiation – Heating Effect



Solvent	Frequency					
	3.10 <sup>8</sup> Hz		3.10 <sup>9</sup> Hz		1.10 <sup>10</sup> Hz	
	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$
water	77.5	1.2	76.7	12.0	55.0	29.7
0.1 M NaCl	76	59	75.5	18.1	54	30
heptane	1.97	-	1.97	0.0002	1.97	0.003
methanol	30.9	2.5	23.9	15.3	8.9	7.2
ethanol	22.3	6.0	6.5	1.6	1.7	0.11
1-propanol	16.0	6.7	3.7	2.5	2.3	0.20
1-butanol	11.5	6.3	3.5	1.6	0.2	-
Ethyleneglycol	39	6.2	12	12	7	5.5
CCl <sub>4</sub>	2.2	-	2.2	0,0009	2.2	0.003

Dielectric properties of solvents

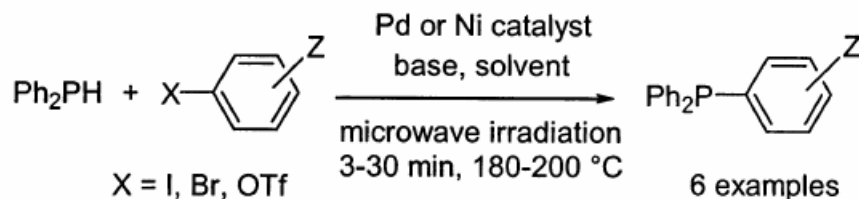
# Microwave Irradiation – Heating Effect



Sample	$P$ (W)	$t$ (min)	$T$ (°C)	Sample	$P$ (W)	$t$ (min)	$T$ (°C)
water	560	1	81	Al	1000	6	577
methanol	560	1	56	C	1000	1	1283
ethanol	560	1	78	Co <sub>2</sub> O <sub>3</sub>	1000	3	1290
acetic acid	560	1	110	FeCl <sub>3</sub>	1000	4	41
CHCl <sub>3</sub>	560	1	49	NiO	1000	6.2	1305
CCl <sub>4</sub>	560	1	28	CaO	500	30	83
acetone	560	1	56	CuO	500	0.5	701
DMF	560	1	131	WO <sub>3</sub>	500	0.5	532
hexane	560	1	25	V <sub>2</sub> O <sub>5</sub>	500	9	701

Temperature change of materials after 2.45 GHz frequency microwave irradiation (RT samples, 50 cm<sup>3</sup> liquid, or 25 g (1000 W) or 5-6 g (500 W) solids)

# Microwave Irradiation – Applications

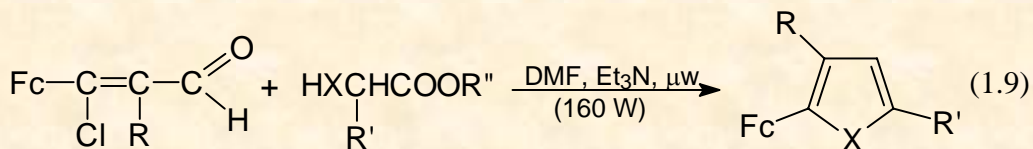


**Table 2.** Microwave-Enhanced Synthesis of Triphenylphosphine from Iodobenzene and Diphenylphosphine Using Pd/C as a Heterogeneous Catalyst<sup>a</sup>

entry	PhI (mmol)	5% Pd/C (mg)	temp (°C)	time (min)	yield (%)
1	0.50	10	190	3	76
2	0.60	10	190	3	93
3	0.75	20	190	3	98
4	0.75	20	200	3	96
5	0.75	20	200	2	96

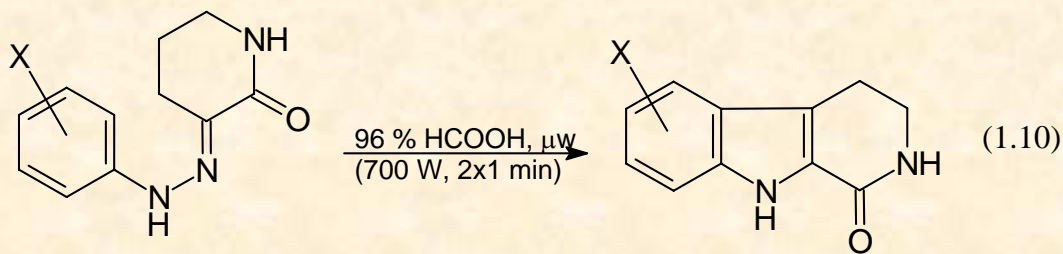
<sup>a</sup> Reactions were carried in DMF (1.0 mL) with 0.50 mmol of  $\text{Ph}_2\text{PH}$  in the presence of KOAc (0.50 mmol). For details, see Supporting Information.

# Microwave Irradiation – Applications



Fc= ferrocenil

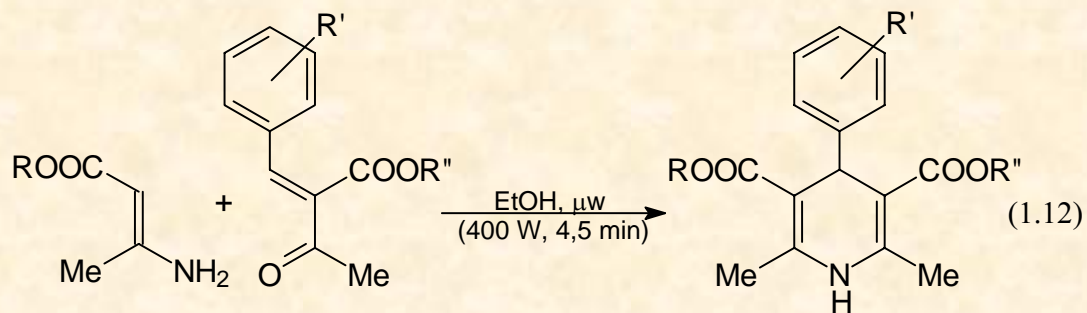
R	R'	R''	X	
H	H	H	S	87 %
Ph	H	H	S	79 %
H	H	Et	O	35 %
H	Ph	H	O	15 %




X= H, 2-Me, 4-MeO,  
4-Br, 4-NO<sub>2</sub>

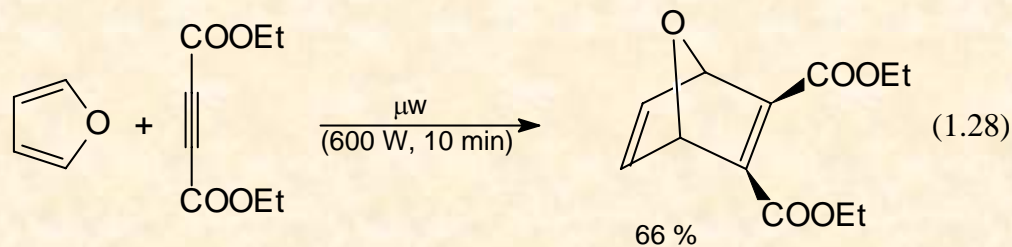
72,8-88 %

# Microwave Irradiation – Applications



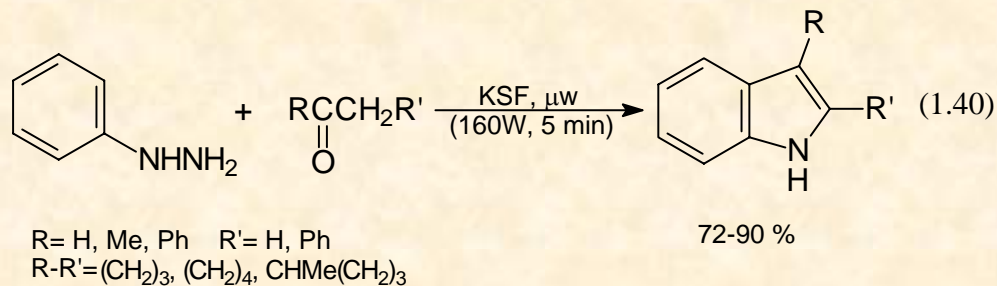
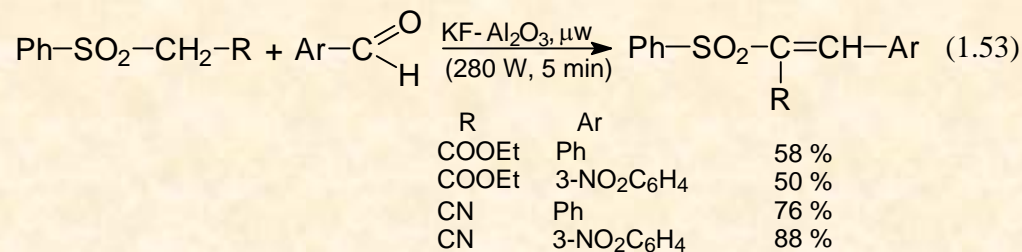
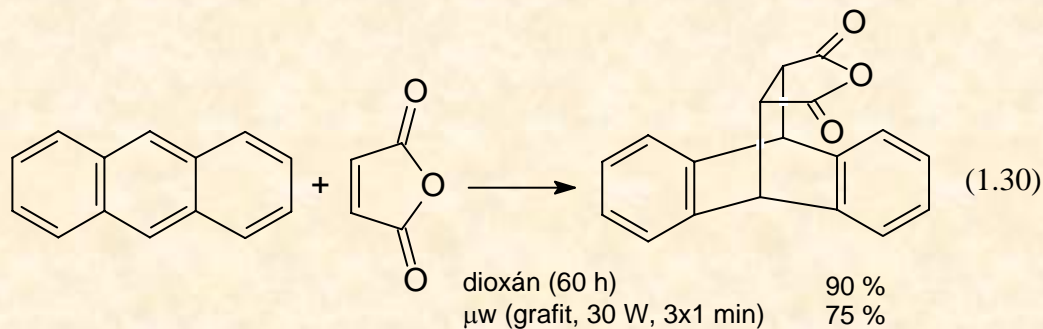
R= Me, iPr, MeOCH<sub>2</sub>CH<sub>2</sub>  
R'= 2- és 3-Cl, 2,3-diCl, 3-Br, 2- és 3-NO<sub>2</sub>  
R''= Me, Et, 

58-98 %

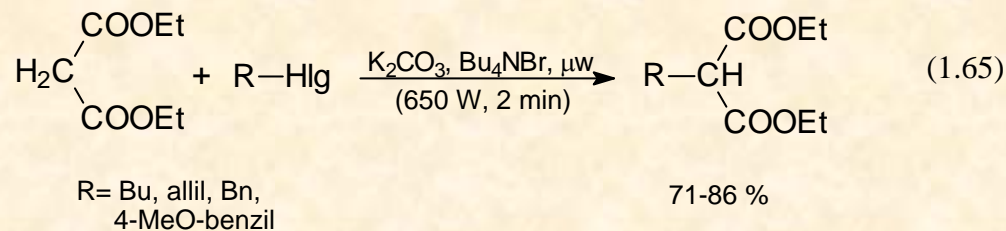
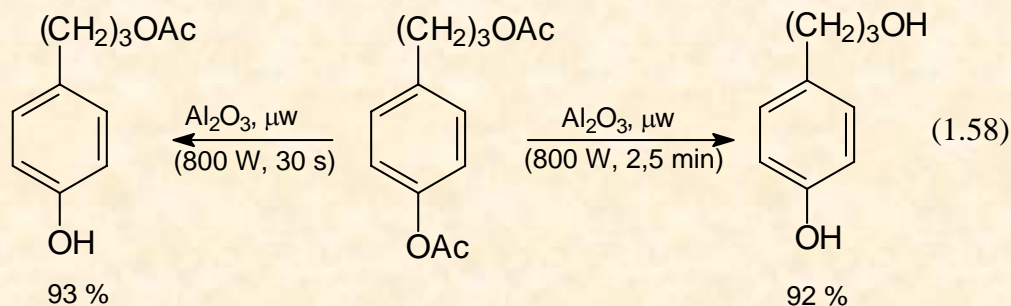


66 %

# Microwave Irradiation – Applications



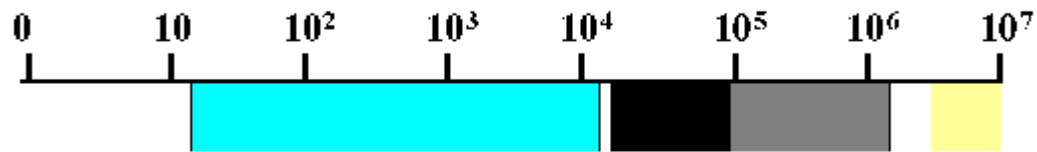
# Microwave Irradiation – Applications



## 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



Human hearing



16Hz - 18kHz

Conventional power ultrasound



20kHz - 100kHz

Extended range for sonochemistry



20kHz - 2MHz

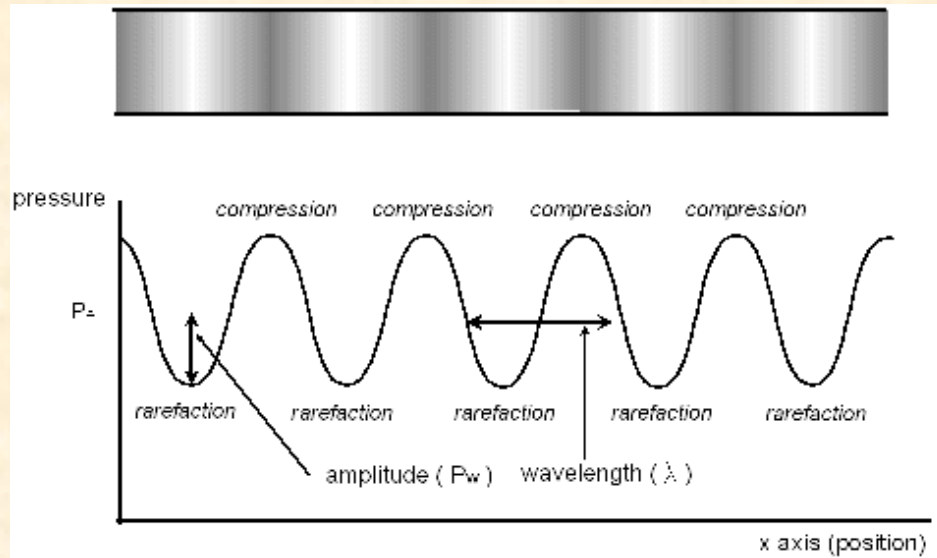
Diagnostic ultrasound



5MHz - 10MHz

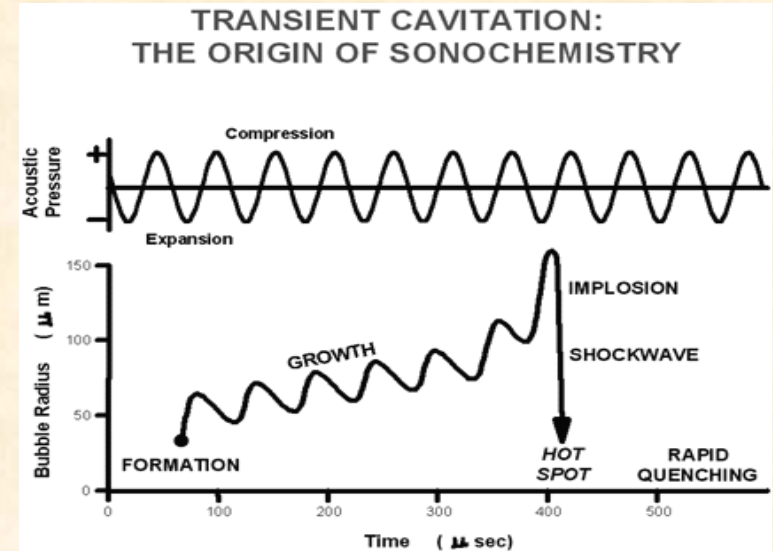
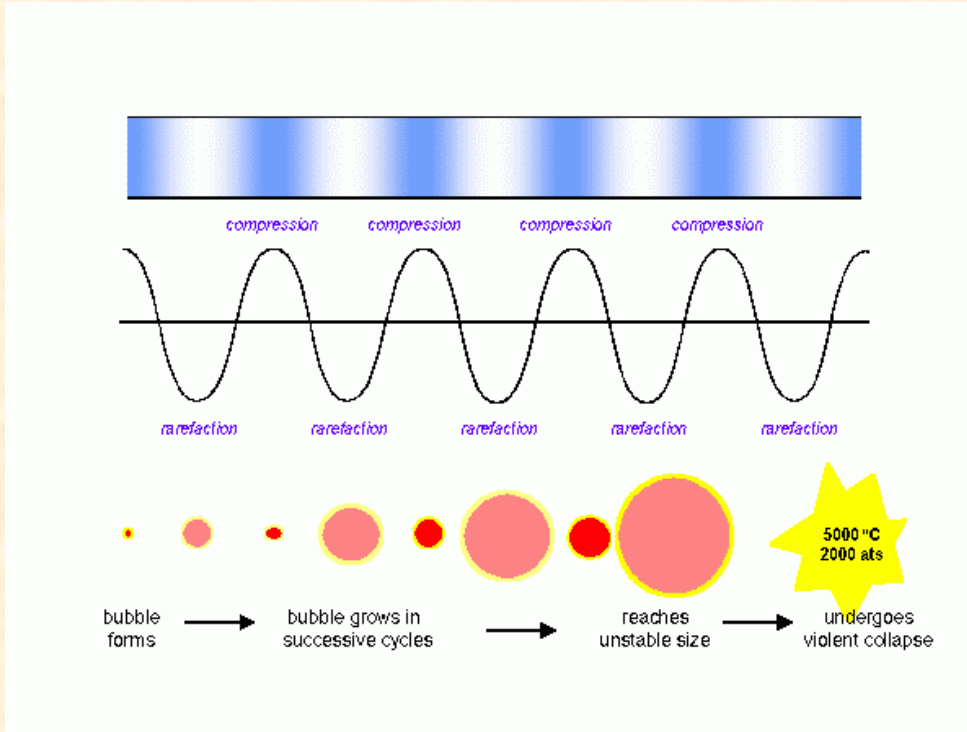
Frequency ranges of sound

# Ultrasonics/Sonochemistry – Basics



Sound transmission through a medium

# Ultrasonics/Sonochemistry – Acoustic Cavitation

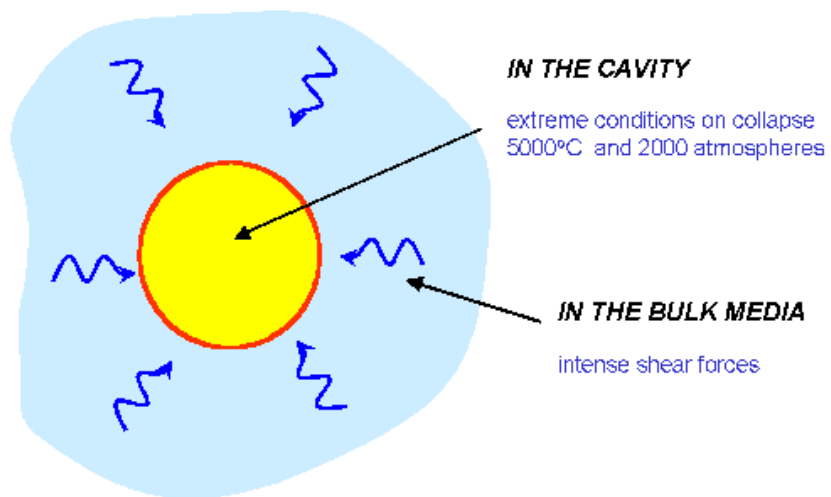


Bubble size and cavitation dynamics

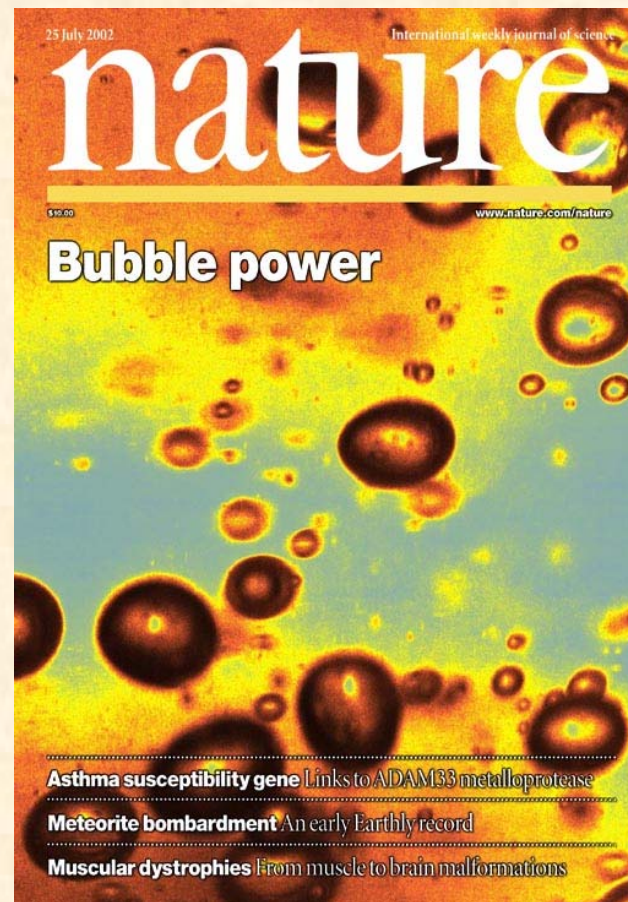
Formation of an acoustic bubble

Transient cavitation

# Ultrasonics/Sonochemistry – Acoustic Cavitation



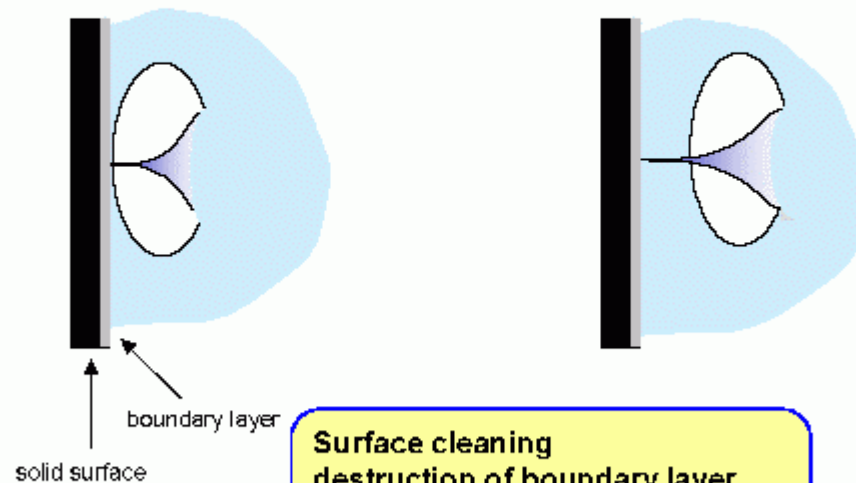
Acoustic cavitation in a homogeneous liquid



Suslick - ~ 4-5000 K

# Ultrasonics/Sonochemistry – Acoustic Cavitation

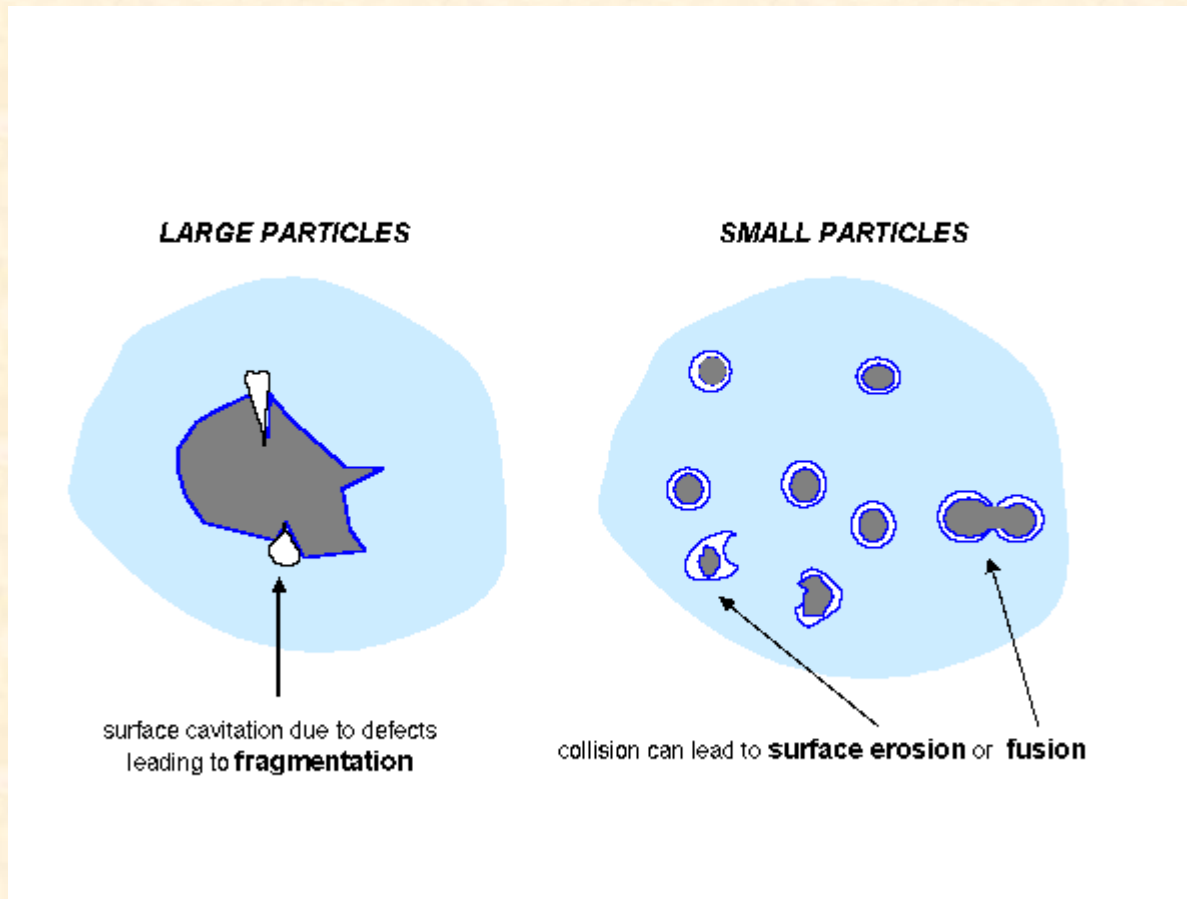
Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface



**Surface cleaning**  
**destruction of boundary layer**  
**surface activation**  
**improved mass and heat transfer**

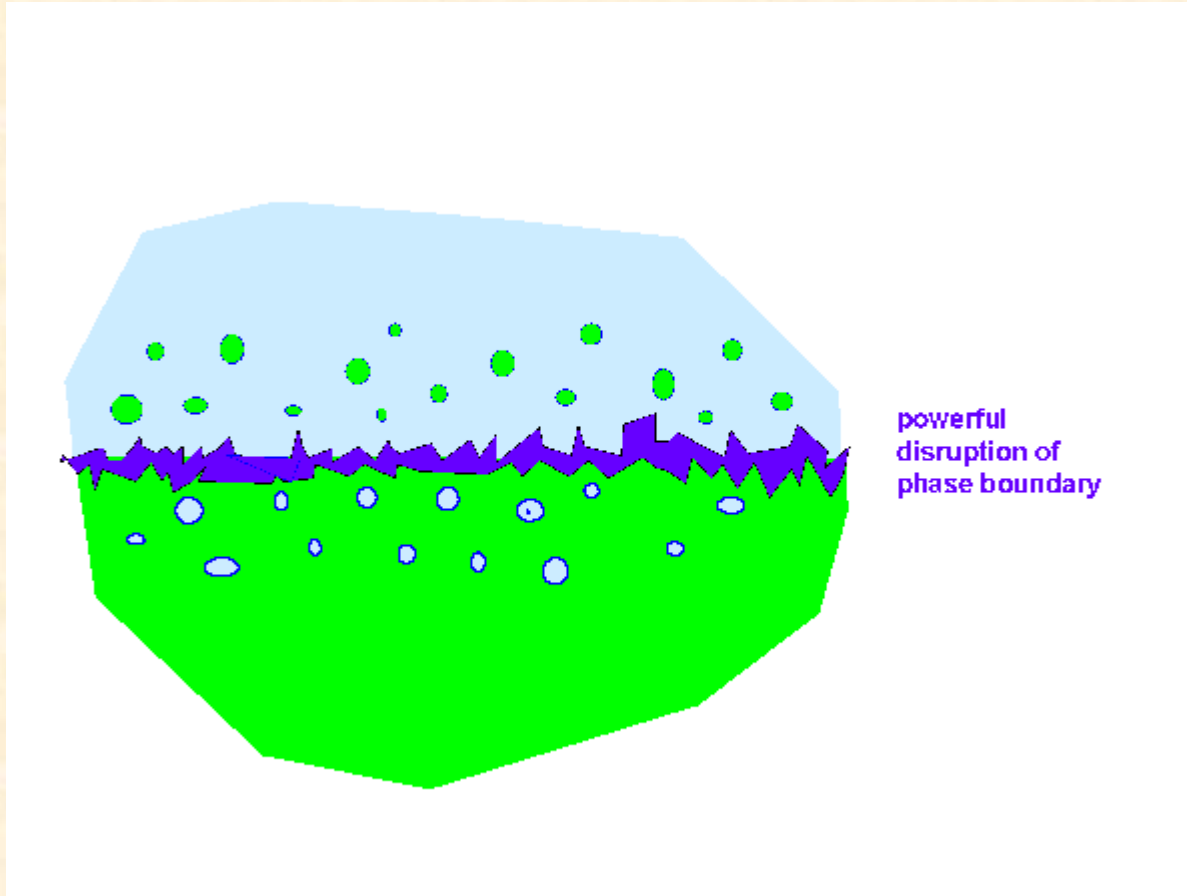
Acoustic cavitation in solid/liquid system

# Ultrasonics/Sonochemistry – Acoustic Cavitation



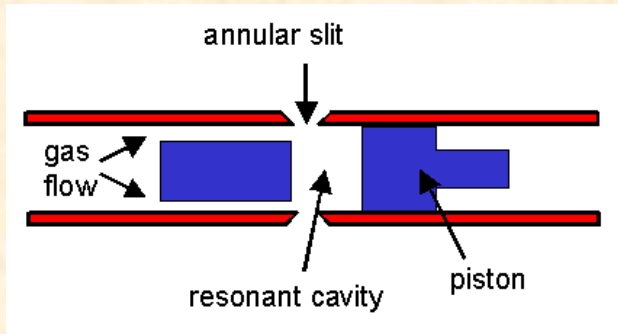
Acoustic cavitation in solid/liquid system

# Ultrasonics/Sonochemistry – Acoustic Cavitation

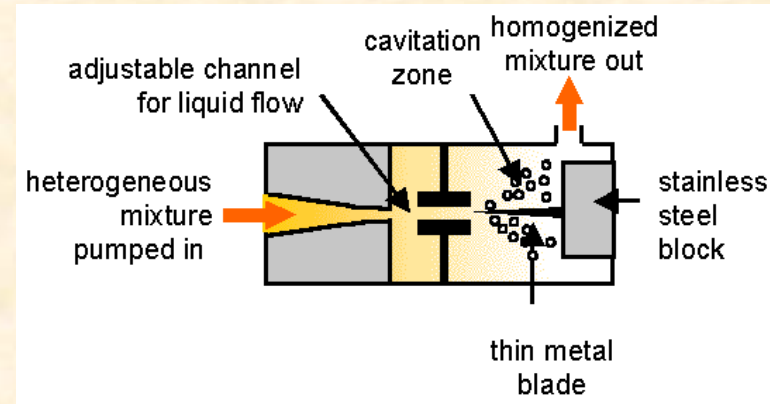


Acoustic cavitation in liquid/liquid system

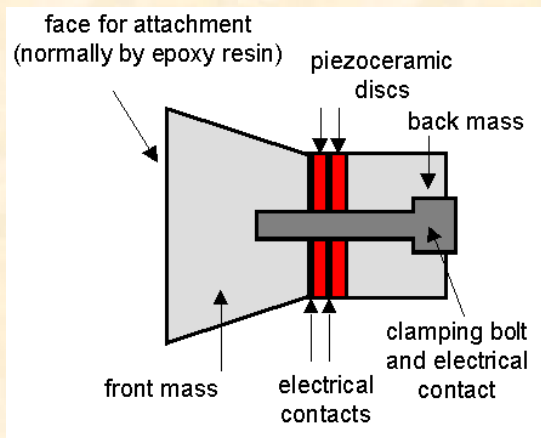
# Ultrasonics/Sonochemistry – Transducers



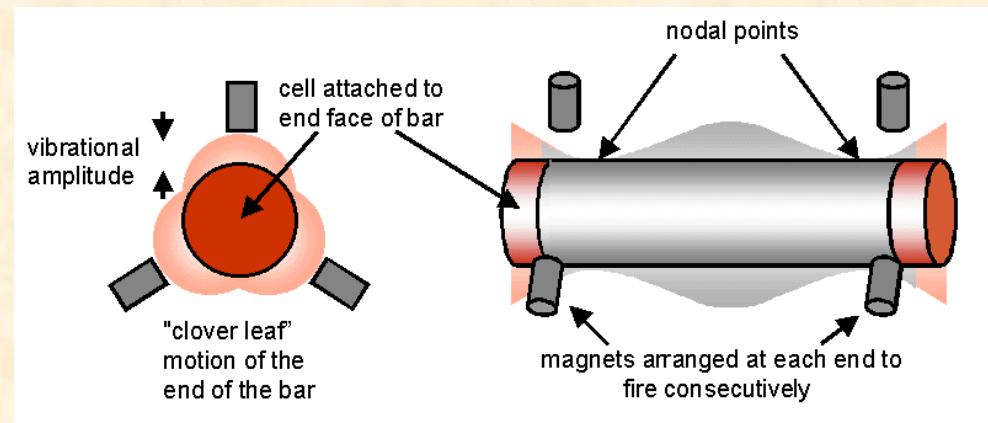
Galton whistle (physical)



Liquid whistle (physical)



Piezoelectric sandwich transducer



Magnetostrictive transducer

# 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 Thermal activation	The content of bubbles, the intensity of collapse Secondary reactions
Static pressure	Total pressure Solubility of gas	Intensity of collapse The content of bubbles
Gas	Politrop ratio Thermal conductivity Chemical reactivity solubility	Intensity of collapse Primer and secondary reactions The content of bubbles
Solvent	Vapor pressure Surface tension Viscosity Chemical reactivity	Intensity of collapse Limit of transient cavitation Primer and secondary reactions

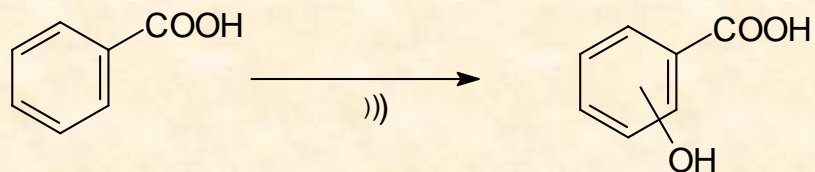
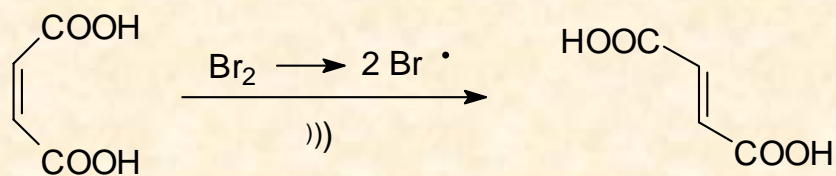
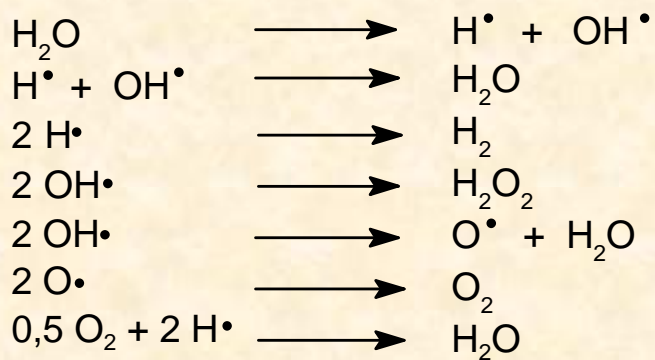
# Ultrasonics/Sonochemistry – Applications



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

# Ultrasonics/Sonochemistry – Synthesis

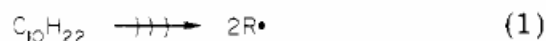
## Aqueous sonochemistry



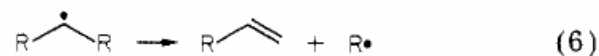
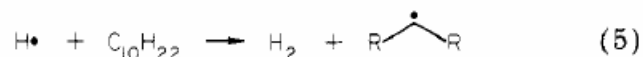
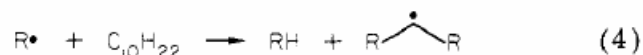
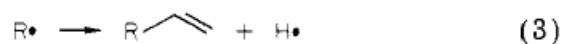
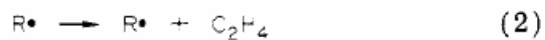
## Non-Aqueous sonochemistry

### Scheme I: Rice Radical Chain Mechanism<sup>a</sup>

initiation:



propagation:

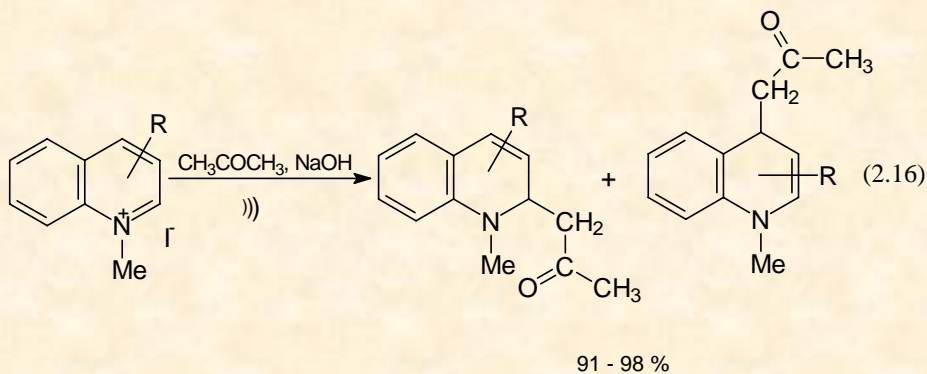
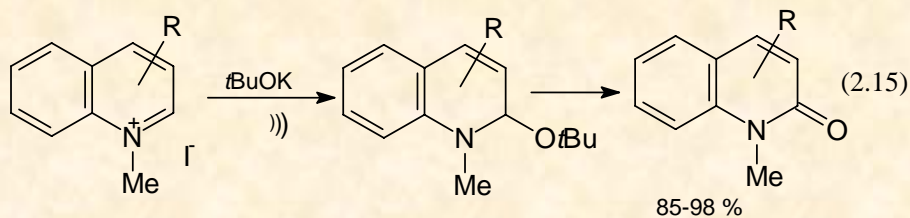
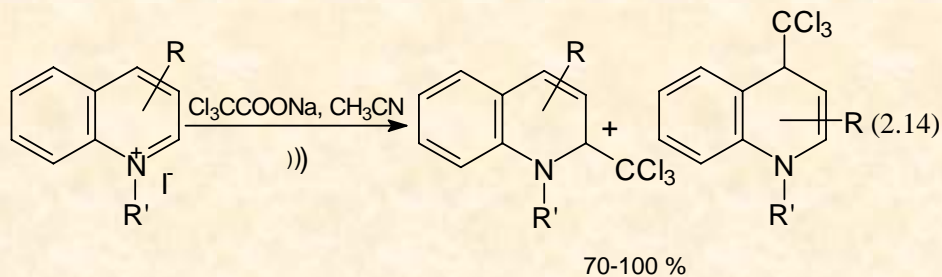


termination:

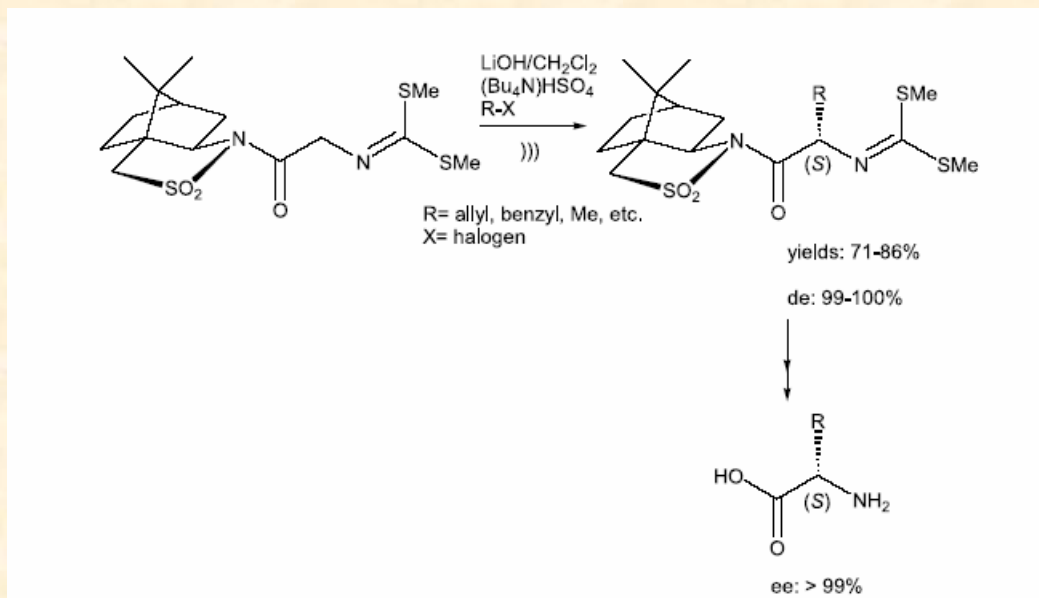
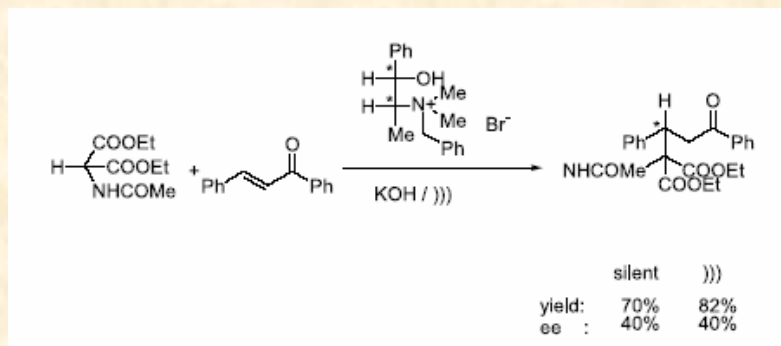


<sup>a</sup>  $\text{R}\cdot$  = terminal radical,  $\text{R}-\dot{\text{C}}\text{H}-\text{R}$  = internal radical.

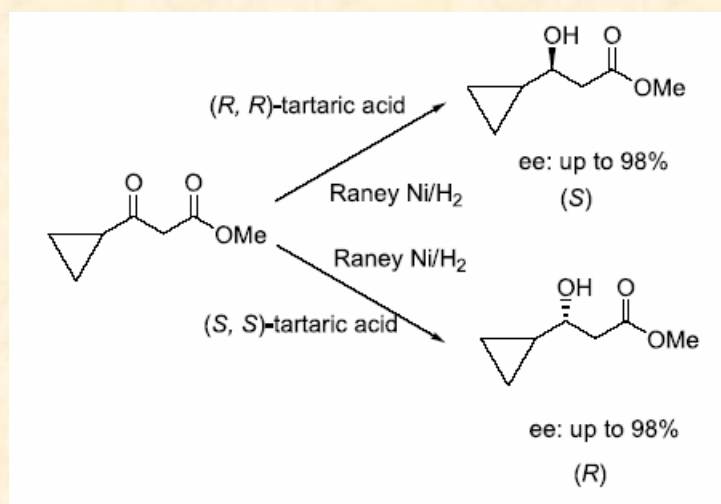
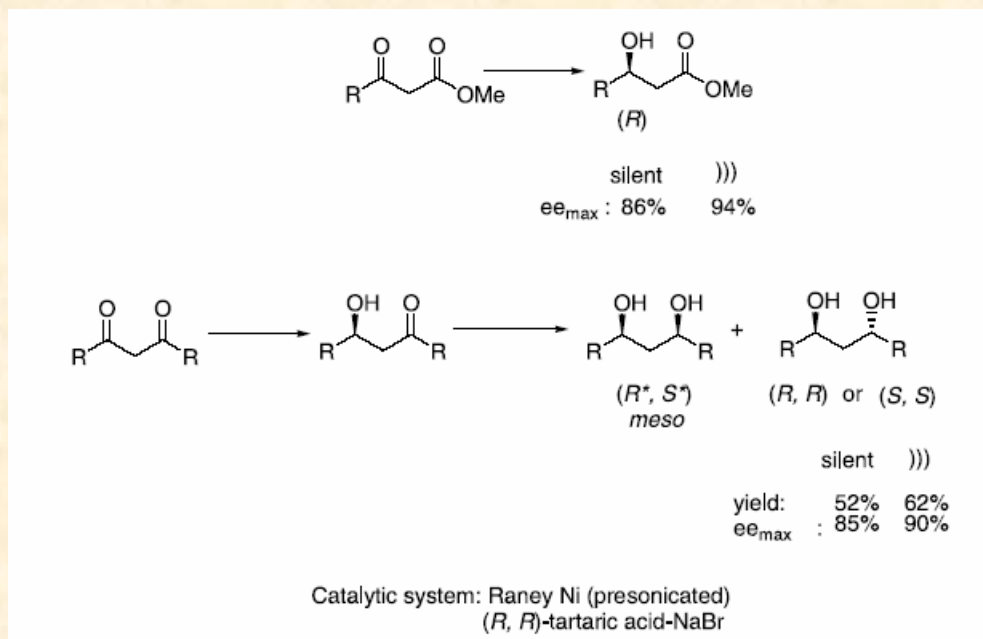
# Ultrasonics/Sonochemistry – Synthesis



# Ultrasonics/Sonochemistry – Synthesis





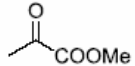
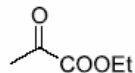
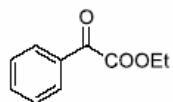
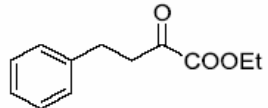
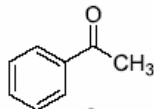
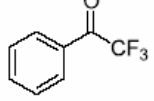
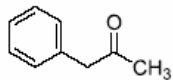
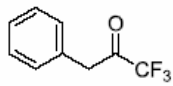
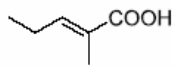
# Ultrasonics/Sonochemistry – Synthesis



# Ultrasonics/Sonochemistry – Synthesis

Table 4

Sonochemical and silent enantioselective hydrogenation of activated ketones, ketoesters and unsaturated carboxylic acids over 5% Pt/Al<sub>2</sub>O<sub>3</sub> (C=O double bond) and 5% Pd/Al<sub>2</sub>O<sub>3</sub> (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	<i>R</i>	94	95
	CD	E40655	10	AcOH	<i>R</i>	85	97
	MeOHCD	E40655	10	AcOH	<i>R</i>	78	98
	CD	E4759	10	AcOH	<i>R</i>	88	92
	CD	E4759	10	AcOH	<i>R</i>	79	96
	CN	E4759	10	AcOH	<i>S</i>	85	92
	CD	E4759	10	DCB	<i>R</i>	6	8
	CD	E4759	10	DCB	<i>R</i>	46	49
	CD	E4759	10	DCB	<i>R</i>	7	8
	CD	E4759	10	DCB	<i>R</i>	18	18
	CD	E40692	50	Toluene	<i>S</i>	50	62

DCB – 1,2-dichlorobenzene.

# Microwaves/Sonochemistry – References

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