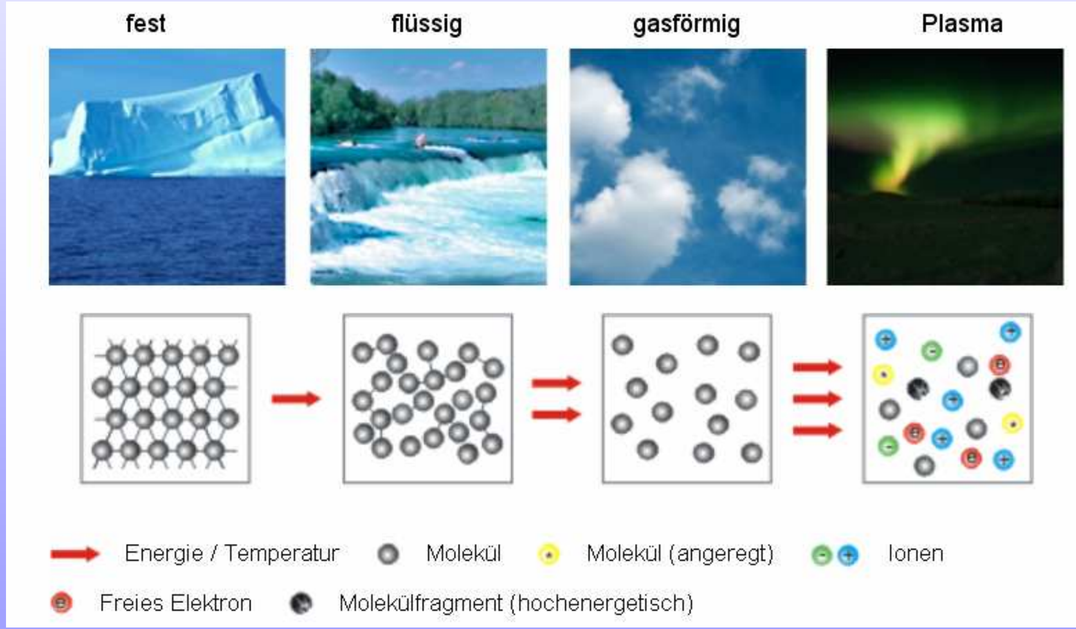
Plasma chemistry

Seminar 13.06.2011
Lena Möller



Reviews

Plasma Modification of biodegradable polymers: A review
Plasma Process Polym **2011**,*8,* 171-190.

Macromolecular plasma-chemistry: am emerging field of polymer science
Prog Polym Sci **2004**, *29*, 815-885.

Atmospheric pressure plasmas: A review
Spectrochimica Acta Part B, **2006**, *61*, 2-30.

Applied plasma medicine
Plasma Process Polym **2008**, *5*, 503-533.

Content

- **Principles**:

What is plasma?

Is there only one form of plasma?

What happens to surfaces?

- **Applications:**

What is plasma good for in industry?

Plasma chemistry in tissue engineering?

- **Conclusions**

Principles:

What is plasma?

- Plasma: “the forth state of matter”
- 99% of universe
- Generated by applying high energies to a gas (thermal energy, electric fields)
- Consists of electrons, ions, neutrals (fundamental or exited states)

  → in total: electrically neutral

  → contains free charge carriers: electrically conductive

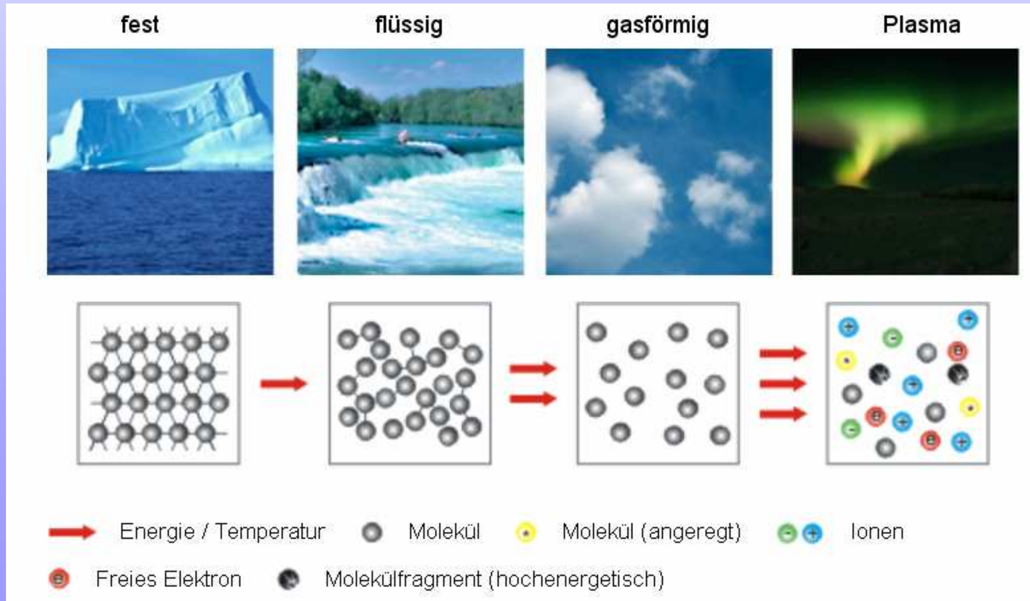


Photo: www.plasmatreat.de

Principles:

What is plasma?

- Plasma consists of electrons, ions, neutrals (fundamental or exited states)
- Electrons faster than ions, neutrals… due to lower mass
  → faster and contain higher temperatures
- In every gas: small percentage of charged molecules: acceleration to induce collisions
- Elastic collisions between e^- and heavy atoms (ha): only kinetic energy is transferred
- Inelastic collisions: excitation or ionization takes place, temperature of ha increases

Spectrochimica Acta Part B, **2006**, *61*, 2-30.

Principles:

Is there only one form of plasma?

- Two different forms of plasma distinguised: thermal and non-thermal plasma: (depending on type and amount of appl. energy)
  → differentiation not precise

T_e = temperature of electrons T_{ha} = temperature of heavy atoms

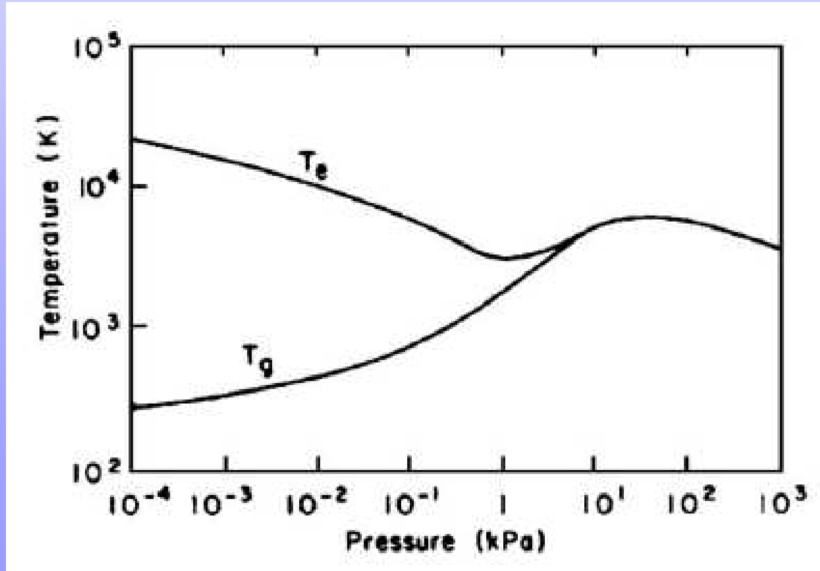
	Thermal plasma	**Non-thermal plasma**
Other names	Hot plasma Near equilibrium plasma	Cold plasma Non-equilibrium plasma
Collisions	Elastic and inelastic	Inelastic (without T transfer)
Temperature	$T_e \approx T_{ha} \approx$ 10,000 K	$T_e \approx$ 100,000 K-10,000 K $T_{ha} \approx$ 300-100 K
Degree of Ionisation	100 %	10^{-4}-10%
e^--density	10^{21}-10^{26} m^{-3}	<10^{19} m^{-3}
	→ No use in thermo-sensitive substrates	→ $T_{ambience} \approx T_h$ useful for thermosensitive appl.

Spectrochimica Acta Part B, **2006**, *61*, 2-30.

Principles:

Is there only one form of plasma?

- Differences in preparation
- Low pressure plasma (vacuum)
  → non-thermal, only inelastic collisions between e^- and ha lead to exciting or ionization, no temperature transfer
- Atmospheric plasma
  → plasma becomes more thermal (inelastic and elastic collisions)
- Dependence on feeding power:
  → high power: thermal plasma
  → low power: non-thermal



Non-thermal plasma ←

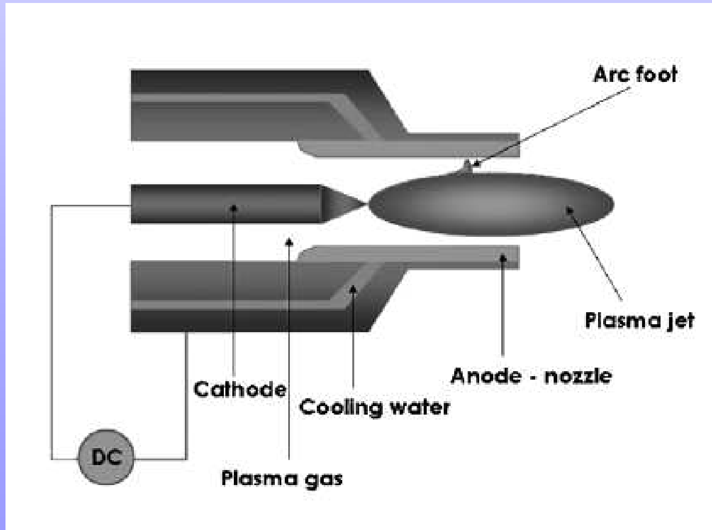
→ Thermal plasma

Spectrochimica Acta Part B, **2006**, *61*, 2-30.

Principles:

Is there only one form of plasma?

- Atmospheric plasma
  → two different zones in plasma:
  Central zone: thermal
  Peripheral zone: non-thermal
- Advantages: Atmospheric plasma
  → in-line production (no vacuum needed)
- Advantages: Low pressure plasma
  → higher plasma range (surfaces of 3D corpora)



Spectrochimica Acta Part B, **2006**, *61*, 2-30.

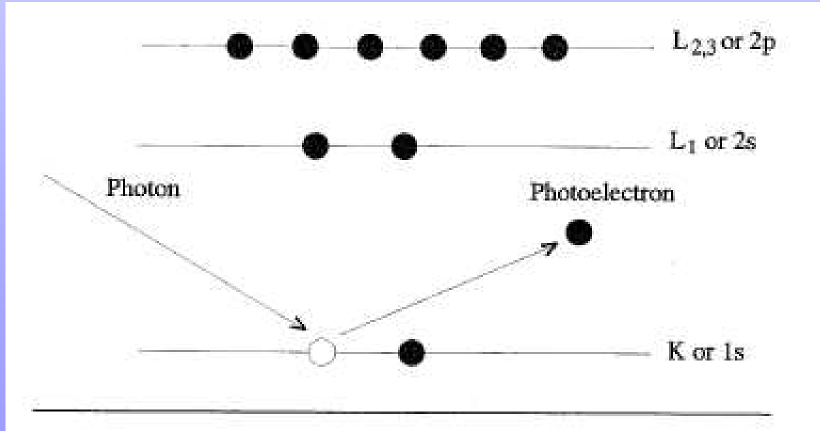
-Insertion: XPS spectroscopy-

- Analysis of plasmamodified surfaces with XPS spectroscopy
- Through irradiation of X-rays to the material, inner electrons (1s, 2s) leave their orbitals (photoionisation)

→ kinetic energy of them is detected, binding energy can be calculated:

$E_{binding} = h\upsilon - E_{kinetic} - \phi_{spektrometer}$ (normaly: $h\upsilon$=1253.6 eV)

→ conculsions can be drawn to the molecules on the surface



J. F. Moulder, W. F. Strickle, P. E, Sobol, K. Bomben, J. Chastain (editor) *Handbook of photoelectron spectroscopy* 2nd Edn; Perkin-Elmer Corporation (Physical Electronics), Minnesota **1992**.

Principles:

What happens to surfaces?

- What happens to the surface during plasma modifications?

⟶ Change of elementary composition of the polymer (here: PLA) dependent the used ionisation gas

Treatment	C at.-%	O at.-%	N at.-%
No	68.2	31.8	0
Air plasma	62.2	37.8	0
Nitrogen plasma	62.1	31.1	6.8
Argon plasma	65.1	34.9	0
Helium plasma	66.9	30.4	2.7

Surf. Coat. Technol **2010**, *204*, 3272.

Principles:
What happens to surfaces?

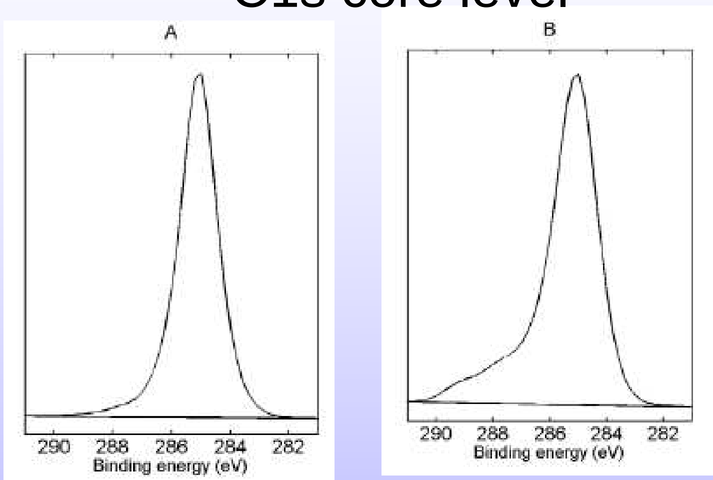
- What happens to the surface during plasma modifications?

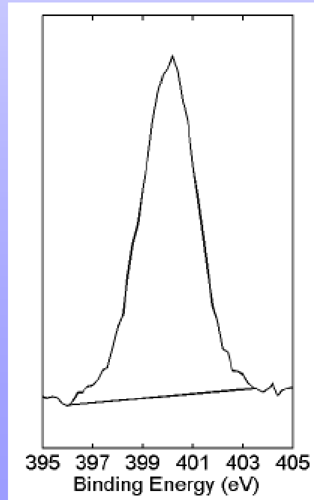
  → Increasing treatment time increases oxygen and nitrogen content (here: N_2 plasma on polypropylenfilms)

  → several forms of carbon nitrogen species detected (amides, imides, nitriles), no nitro, oxime, nitrate groups

Treatment time (s)	O (at%)	N (at%)
0	3.9	0.0
0.25	5.8	1.3
0.75	7.4	3.6
2.00	9.4	8.6
4.00	9.6	10.1

- C1s core level



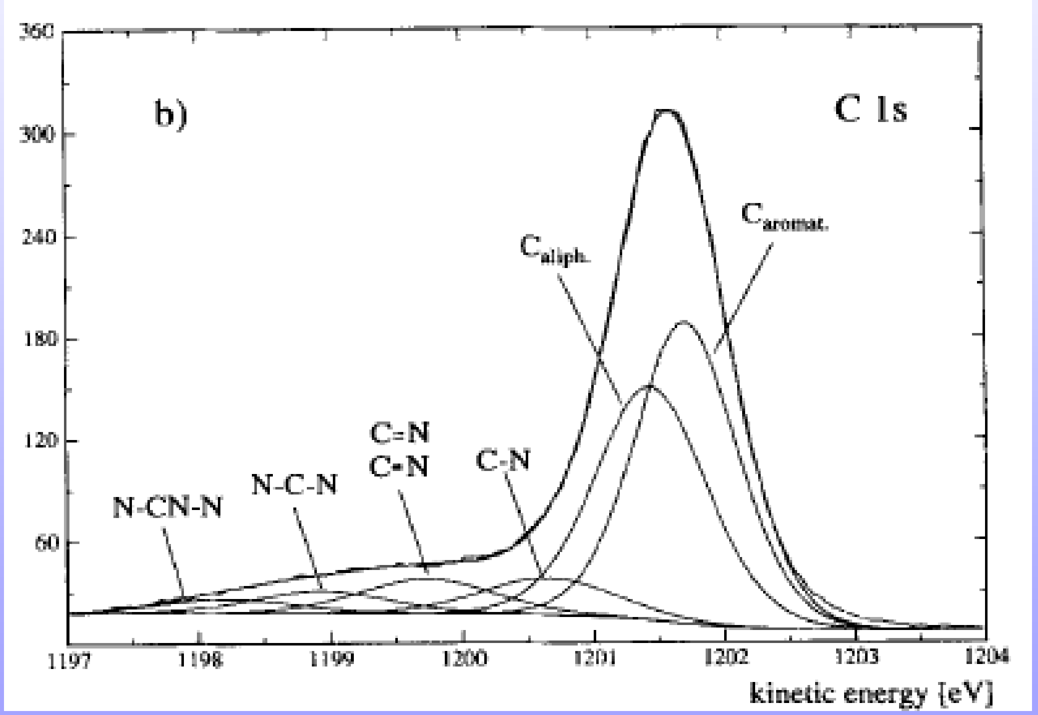


- N1s core level

Eur. Phys. J. Appl. Phys **2008**, *43*, 289-294.

Principles:
What happens to surfaces?

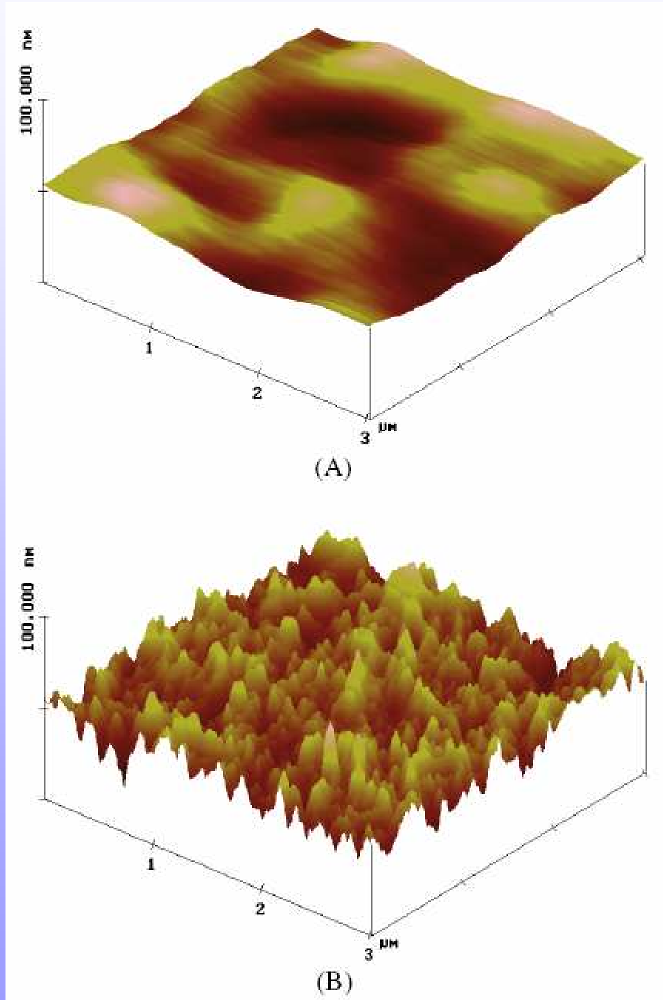
- N_2-plasma treatment of Polystyrene



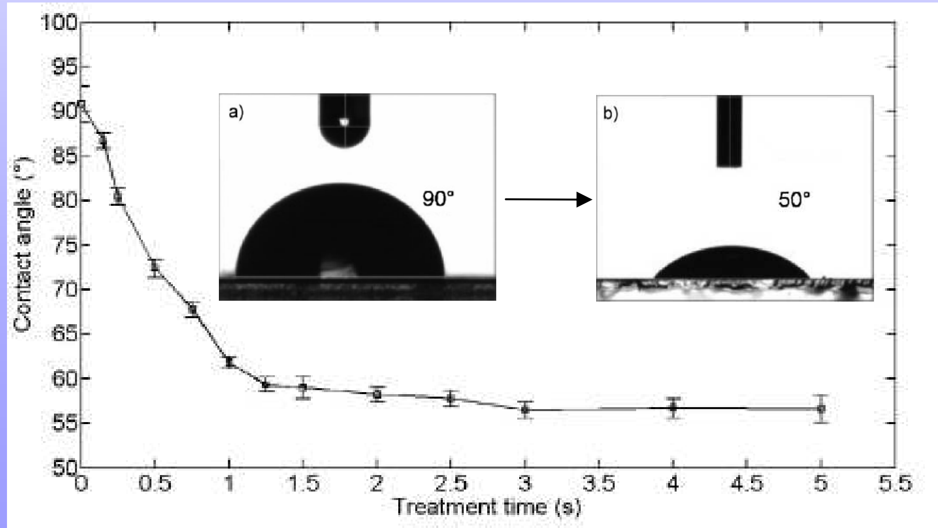
Surf. Interface Anal. **1994**, *21*, 274-282.

Principles:

What happens to surfaces?



- Morphology changes due to plasma treatment: increasing surface roughness (here: N_2 plasma on polypropylenfilms (PP):
- Contact angle decreases



Eur. Phys. J. Appl. Phys **2008**, *43*, 289-294, *J. Appl. Polym. Chem.* **2009**, *114,* 3602.

Applications:

What is plasma good for in industry?

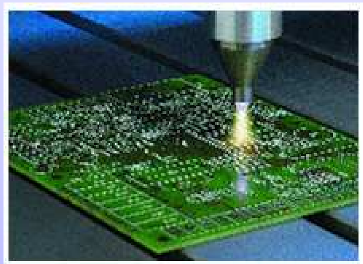
- Many applications:
- surface coatings (pretreatment for printing, varnishing and gluing)

  → cheap glue on the basis of water can be used even for unpolar surfaces
- surface cleaning

  → lubricants from early fabrication steps can be removed before gluing

  → cleaning of sensitive surfaces (LCD-Displays, siliciumwaver)

  → sterilization in medical appl.
- waste destruction, gas treatments, chemical synthesis



Photos:www.plasmatreat.de

Applications:

Plasma chemistry in tissue engineering?

- Why biodegradable polymers in tissue engineering?

  → no second surgcial procedure to remove implant

  → lower risk of re-fracture (bone TE) with successive degradation of the implant

  → potential in drug release
- synthetic, biodegradable (hydrolysable) polymers:

  Esters, anhydrides, ortho-esters, amides
- Advantages:

  Good mechanical properties, low immunogenicity, non-toxicity, adjustable degradation rates
- Disadvantages:

  Low wettability, inefficient cell adhesion, spreading and proliferation

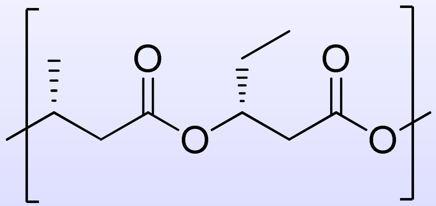
  → Plasma chemistry

Plasma Process Polym **2011**,*8,* 171-190.

Applications:

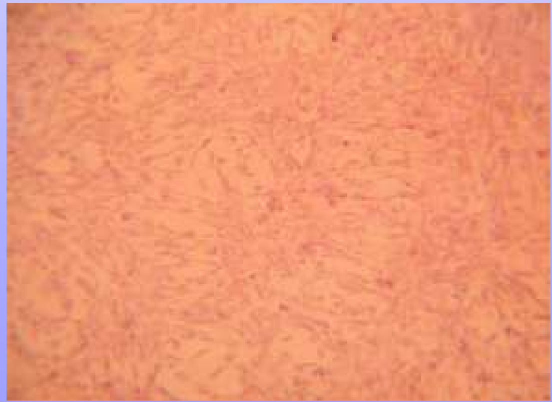
Plasma chemistry in tissue engineering?

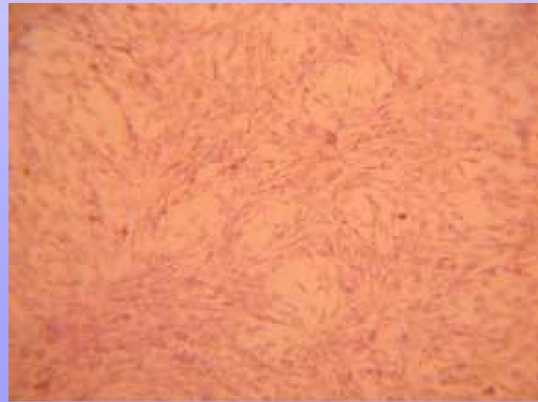
- PHBV in cartilage tissue engineering



→ increased proliferation of dog bone marrow stromal cells after plasma treatment

→ nitrogen and oxygen plasma led to similar biological results even if surface chemistry was different





Biomed. Mater. Res. **2006**, *76a*, 591-595.

Applications:

Plasma chemistry in tissue engineering?

- Plasma is used to further functionalize surfaces:

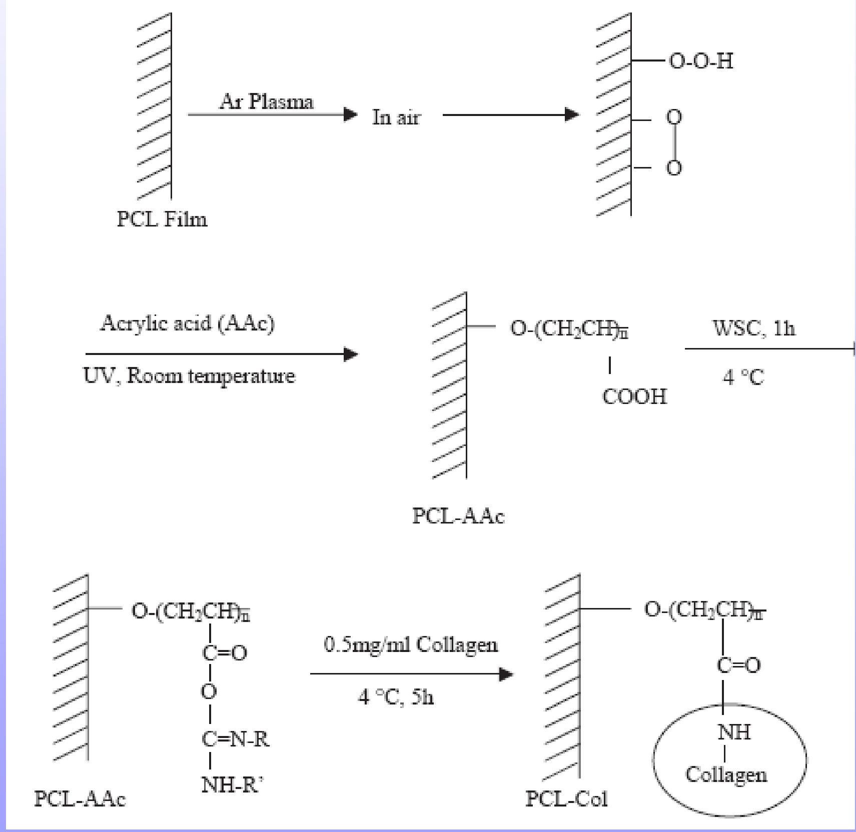
  1. Ar-plasma induces radicals

  2. Surface is oxidized using air

  → peroxides, hydroperoxides

  3. Further polymerisation with acrylic acid

  4. Carbodiimide chemistry to functionalise the surface with biological active substrates such as collagen



Biomaterials **2004**, *95*, 1991-2001.

Conclusion

- **What is plasma?**

  A mixture of electrons, ions, neutrals (fundamental or exited states) generated by applying high energies to a gas
- **Is there only one form of plasma?**

  No, we distingush thermal vs. non-thermal plasma and low pressure vs. atmosheric plasma
- **What happens to surfaces?**

  Change of elementary composition, morphology and wettability
- **What is plasma good for in industry?**

  pretreatment for printing, varnishing and gluing, surface cleaning
- **Plasma chemistry in tissue engineering?**

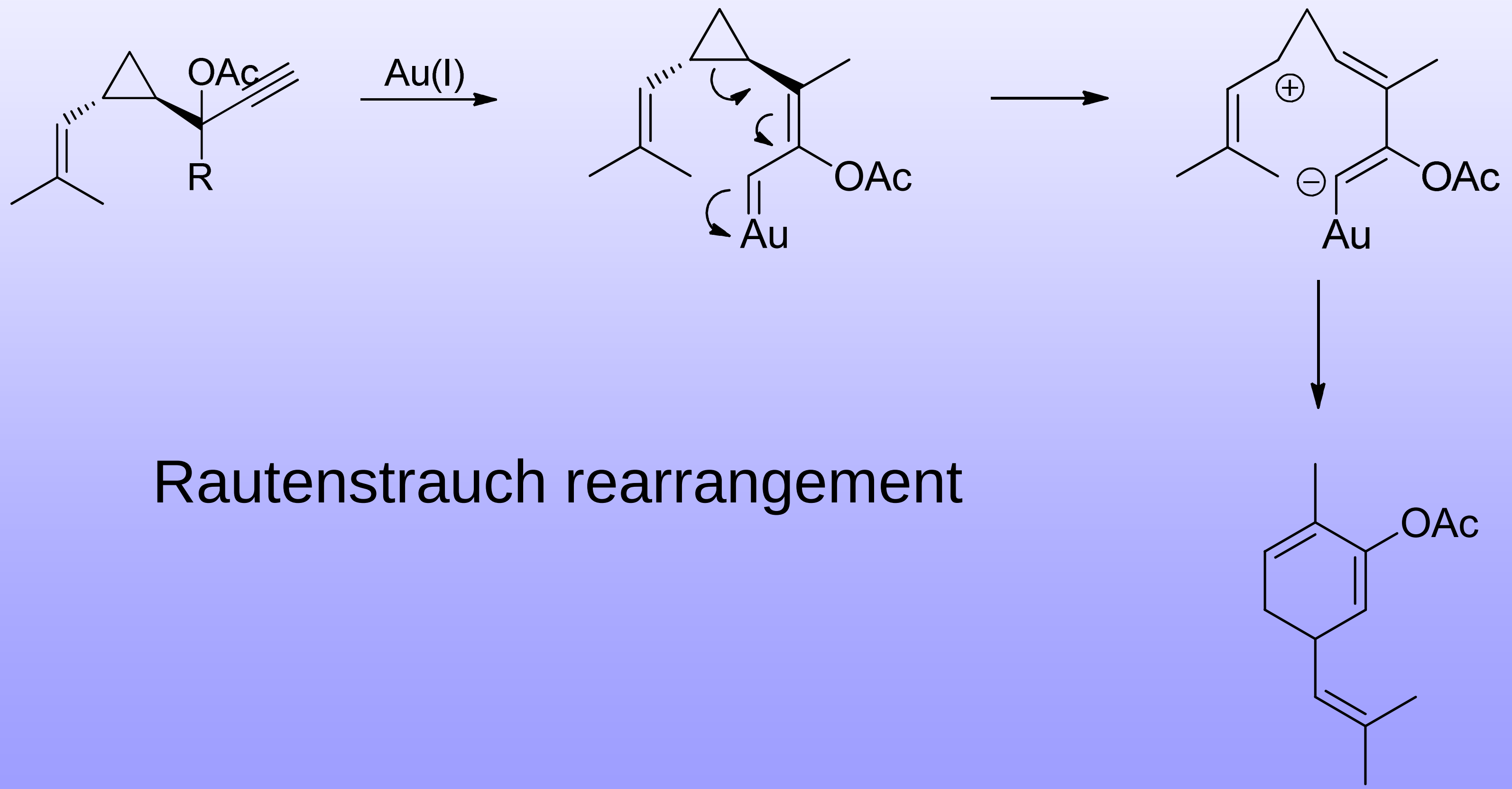
  Plasma enhances wettability and increases cell proliferation; further chemical functionalisation possible

Biomaterials **2004**, *95*, 1991-2001.

Quiz

-Gold and small rings-

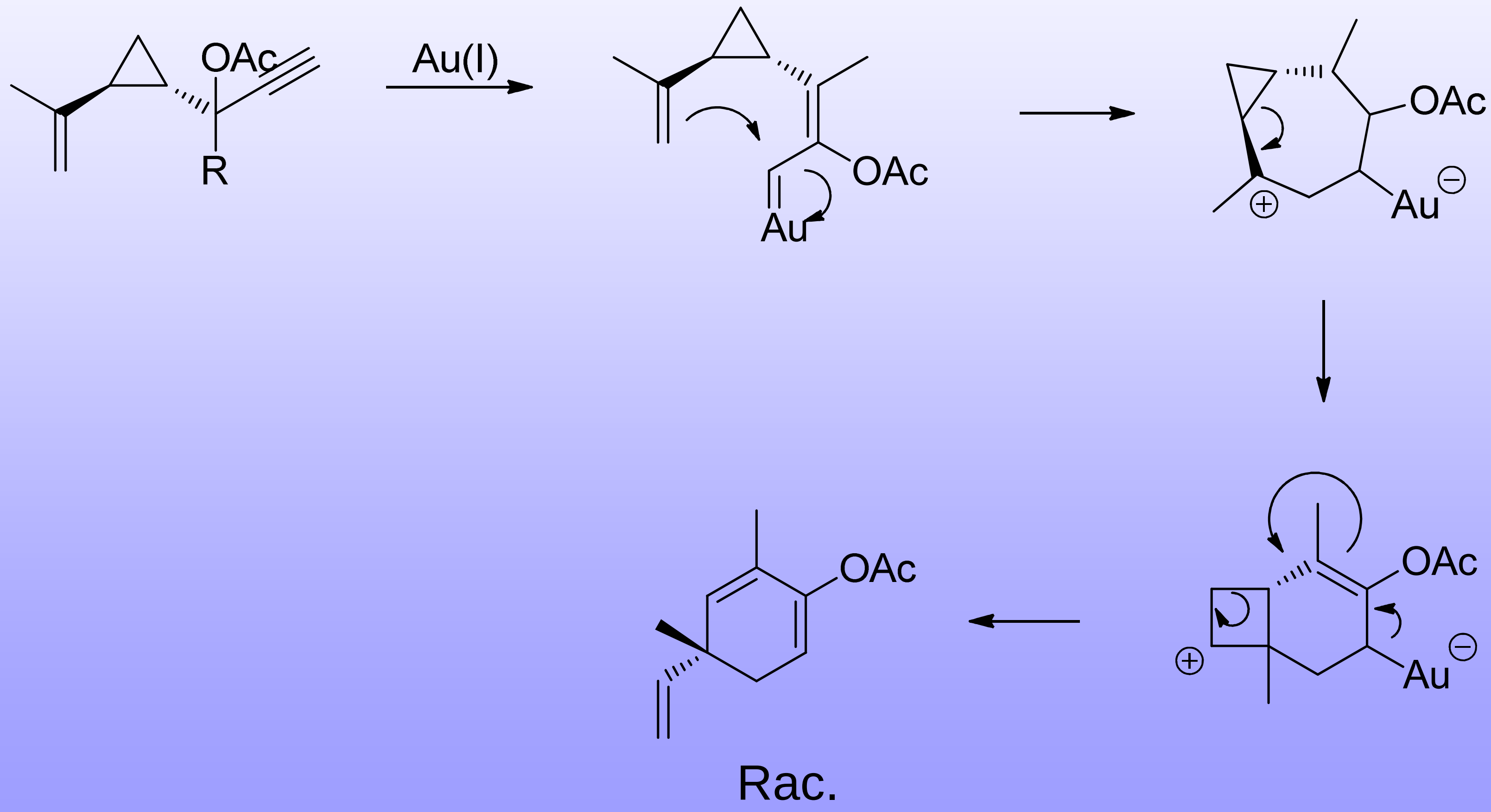
Problem 1



Rautenstrauch rearrangement

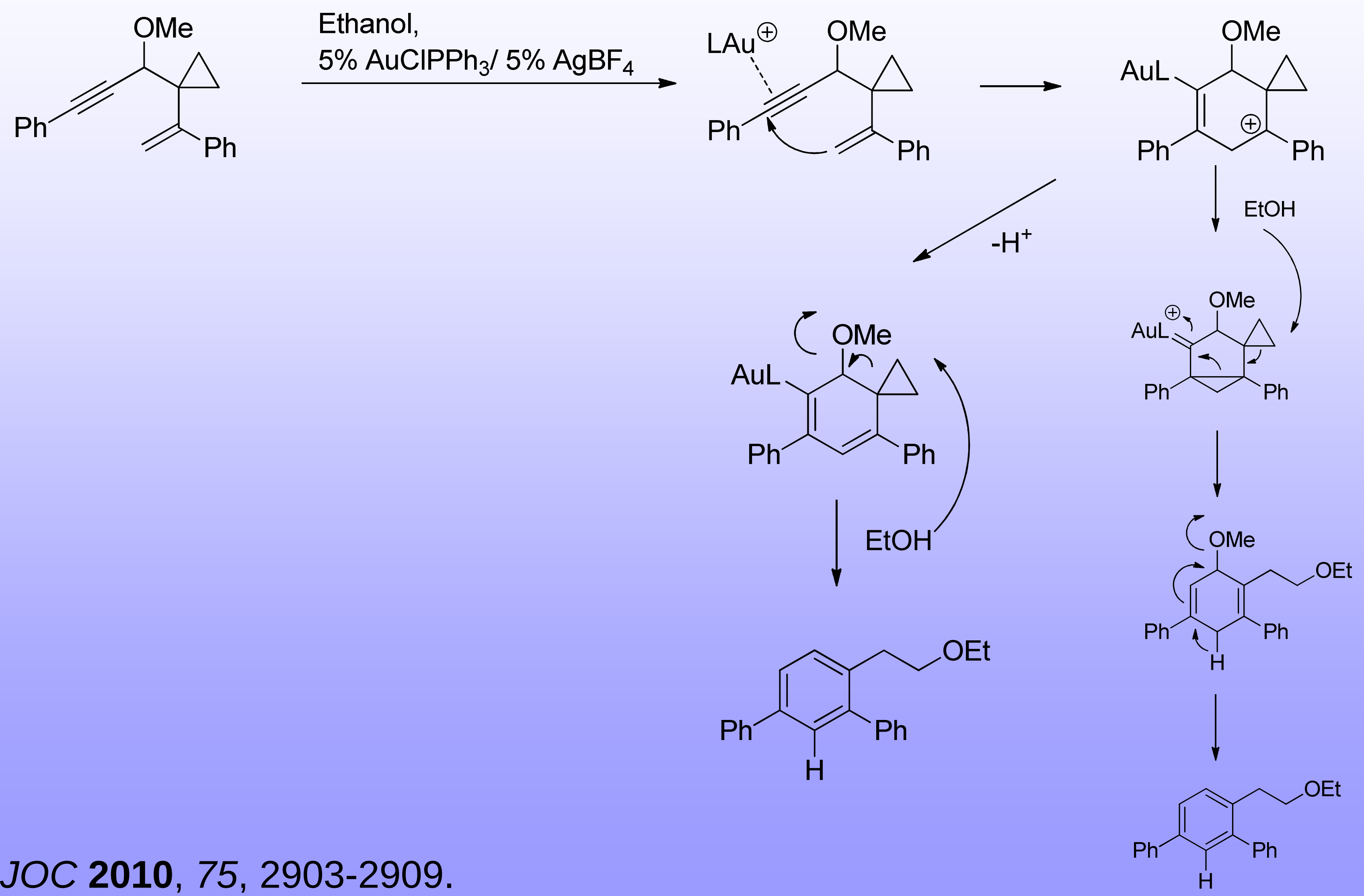
Angew. Chem. **2008**, *47*, 10110-10113.

Problem 2



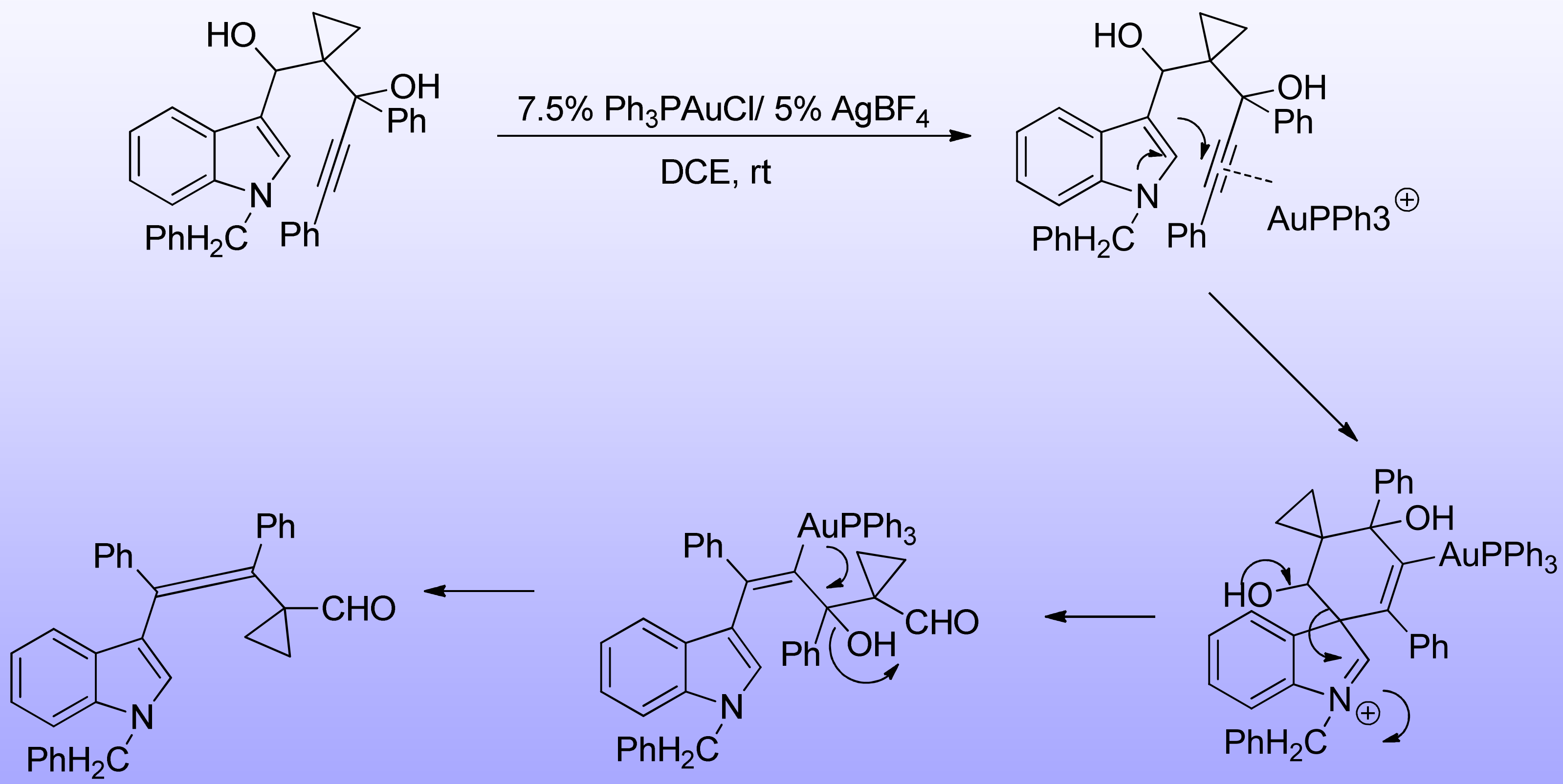
Wang et al. *JOC,* asap

Problem 3

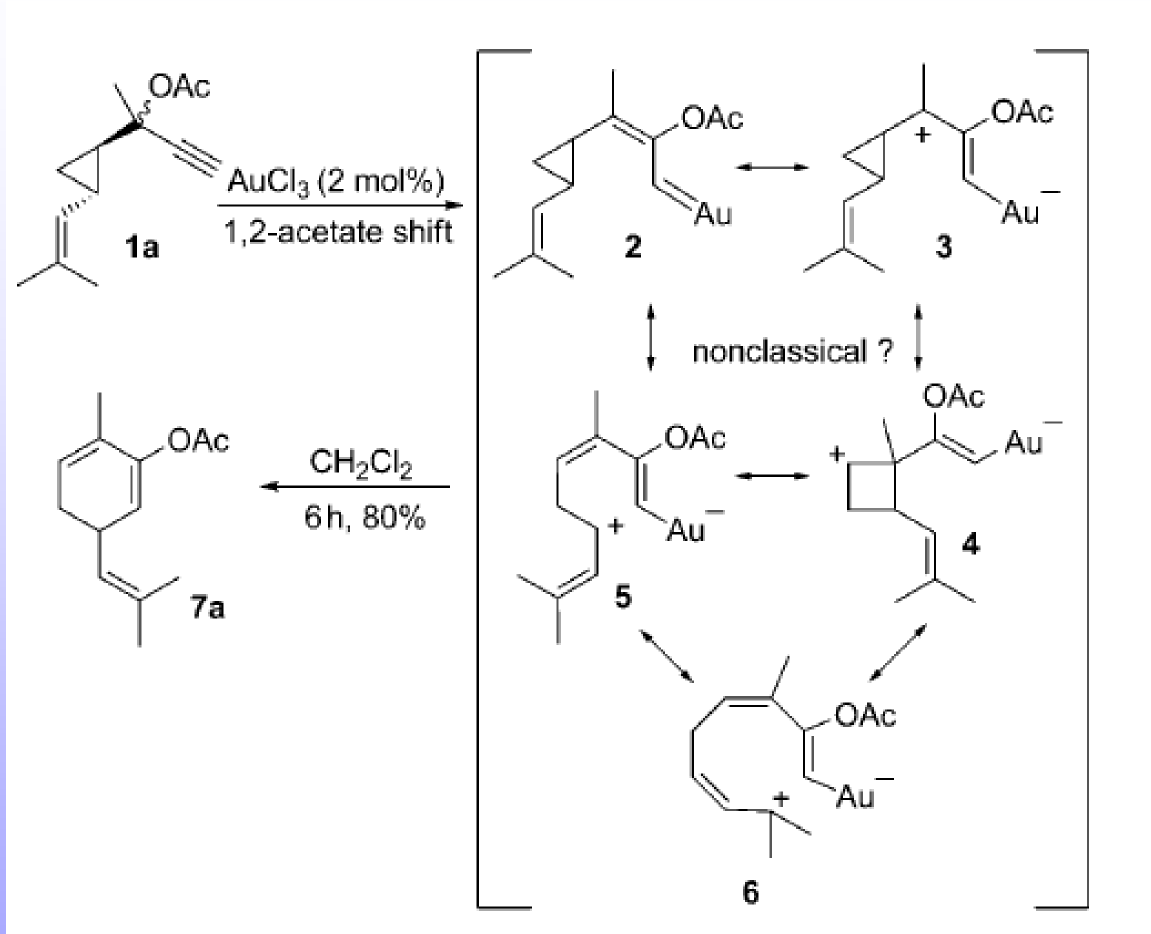


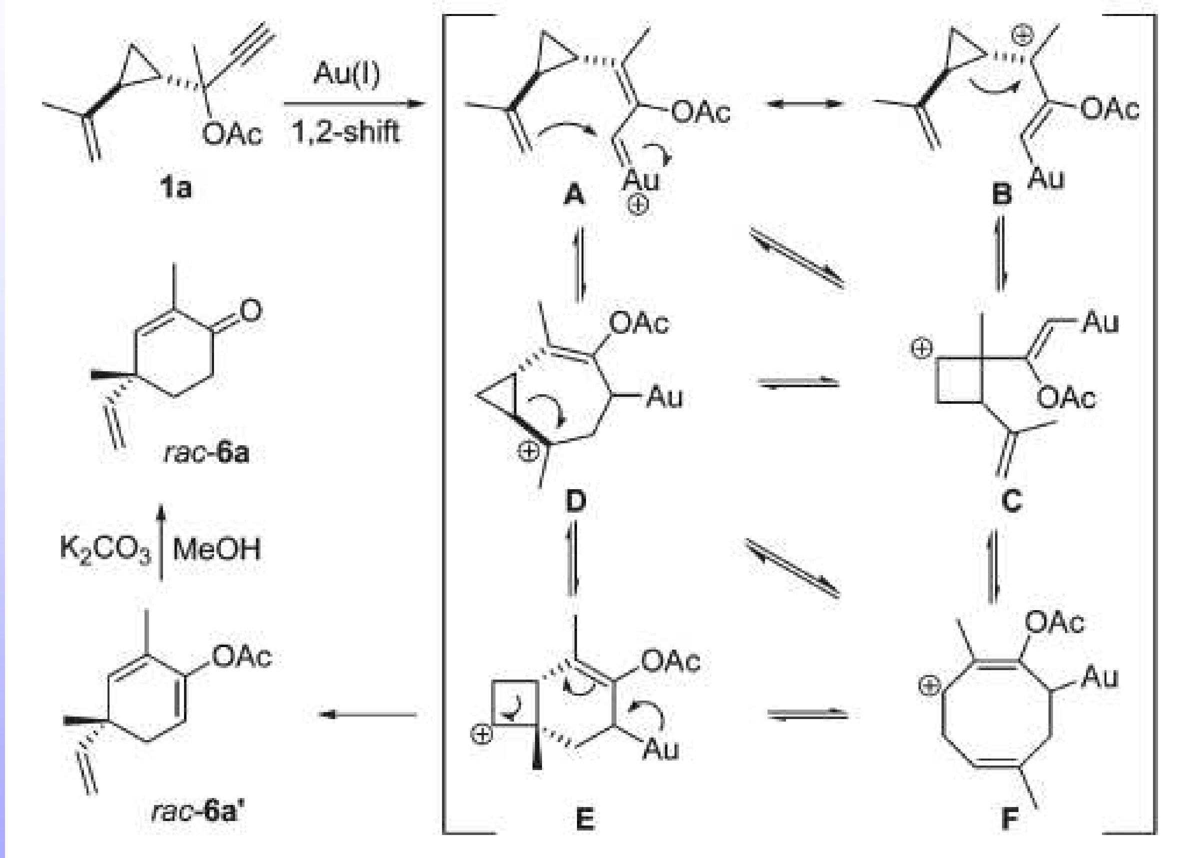
JOC **2010**, *75*, 2903-2909.

Problem 4



JOC **2010**, *75*, 3526-3528.


OAc
AuCl3 (2 mol%)
1,2-acetate shift
1a
OAc
Au
2
+
OAc
Au
3
nonclassical ?
OAc
CH2Cl2
6h, 80%
7a
OAc
+
Au
5
OAc
+
Au
4
OAc
+
Au
6


Au(I)
1,2-shift
OAc
1a
A
B
C
D
E
F
Au
rac-6a
rac-6a'
K_2CO_3
MeOH