Surfactant = Surface Active agent (compound)

Surface or **Interface** : The border between two materials

- extremity thin layer = very small amount (nano world)
- controlled by surface tension (surface free energy)

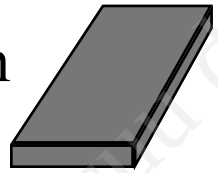
Determine the **looks** of materials

⇩

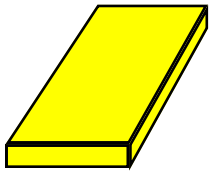
some properties

for example

Iron



Gold plating ⇒



Looks Gold
Strong as Iron

Modification of just surface make the material more worthful.

⇧

Surfactant

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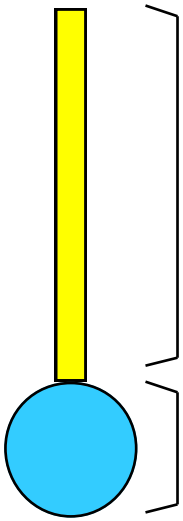
Molecular Structure of Surfactant



Lipophile
(Alkyl chain)

repulsive to H_2O

no affinity

connected with
covalent bond

Hydrophile
(Polarized group)

attractive to H_2O

strange structure

⇩

versatile function

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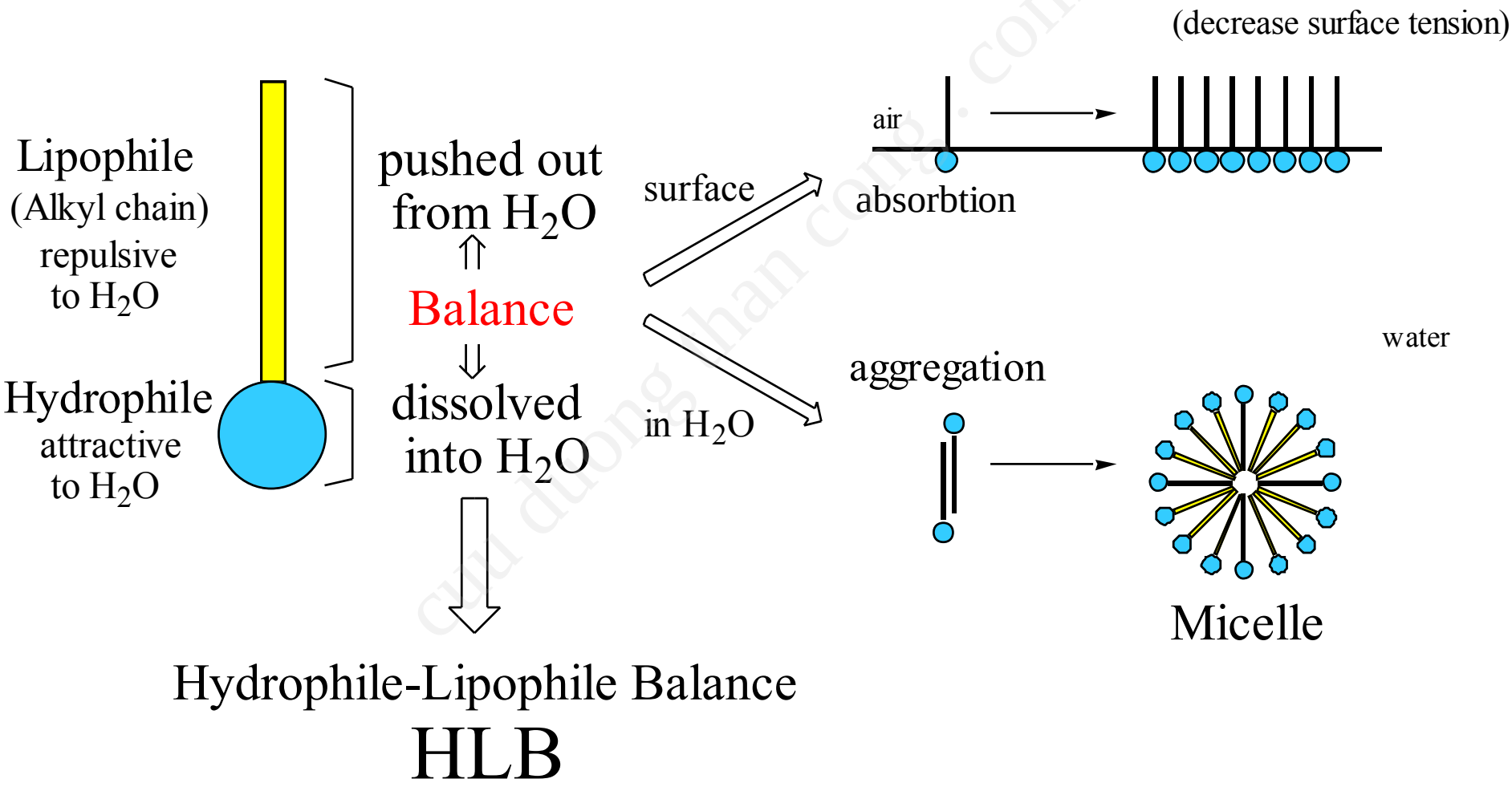
Molecular Assembly of Surfactant



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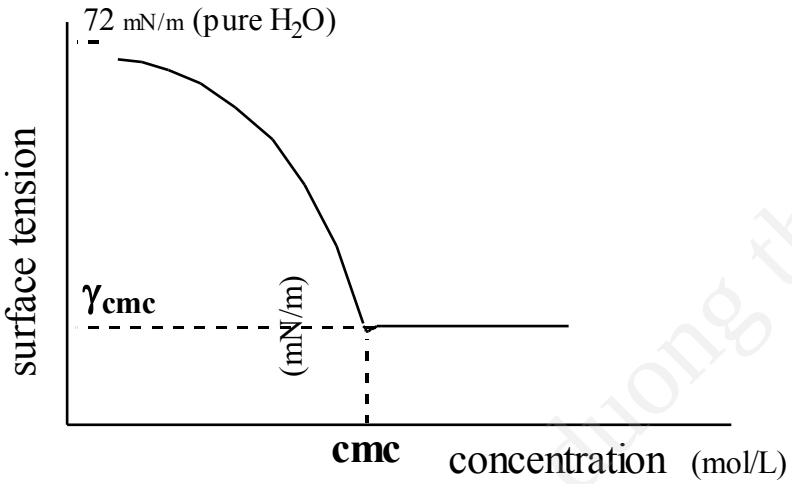
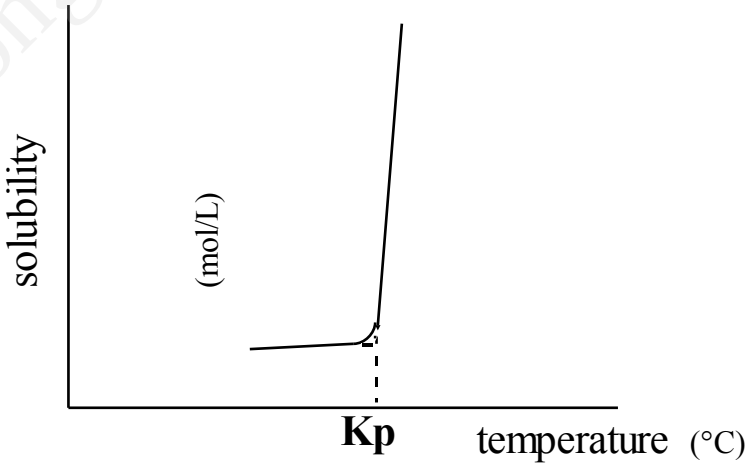
Surface Properties of Surfactant

Surface tension - concentration of H_2O solution



Solubility - temperature of H_2O solution



- Critical Micelle Concentration (**cmc**, mol/L)
  = minimum concentration of surfactant for formation of micelle
- Surface Tension at cmc (γ_{cmc}, mN/m)
  Over cmc, surface tension was kept constant value

- Krafft point (**Kp**, °C)
  Solubility at Kp goes up to cmc

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Surface Properties of Surfactant

Increase Lipophilicity (lengthene alkyl chain) = **decrease** Hydrophilicity

- **cmc**: smaller
  for down sizing
  = good for cost & environment
  ◎ **smaller**
- γ_{cmc}: lower
  high ability of
  lowering surface tension
  ○ **lower**
- **Kp**: **higher** temp.
  wide range of temp. for use
  (below Kp, micelle was not formed)
  × **higher**

Same HLB will suggest same surface properties such as cmc

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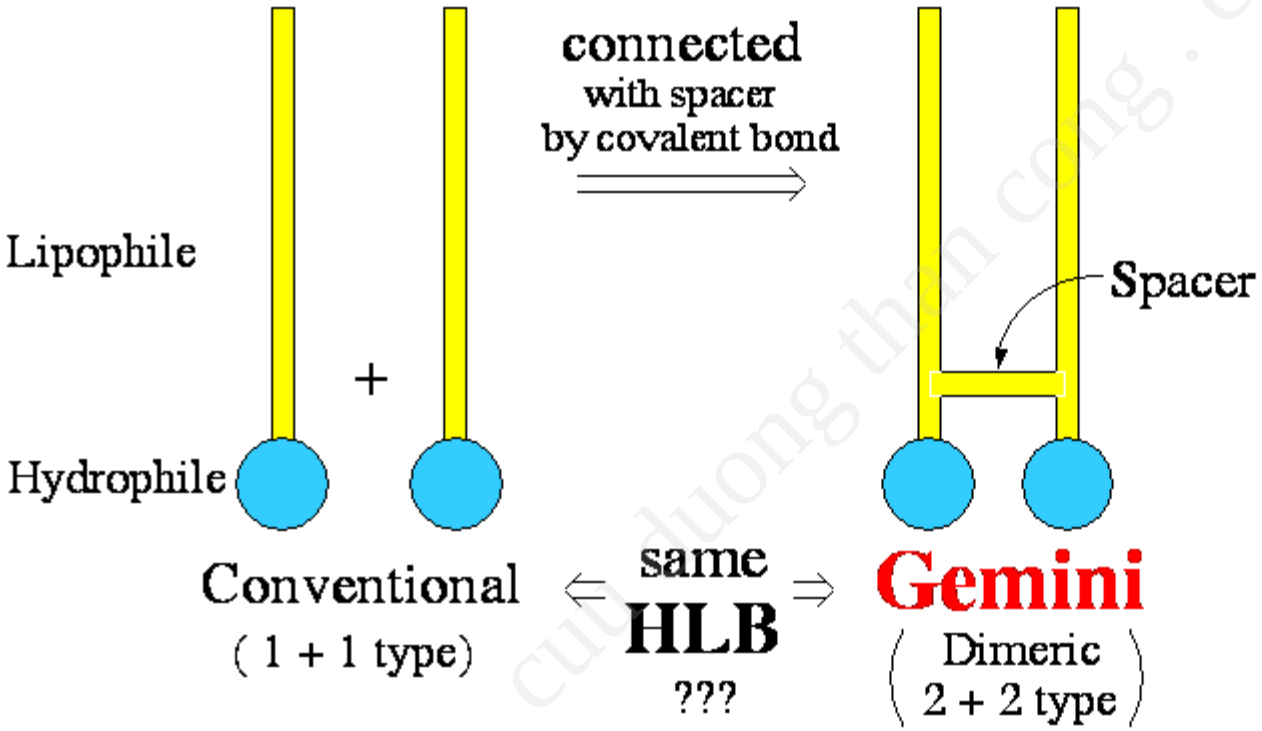
Next Generation of Surfactant



Novel Structure

⇒ Fascinating surface propeties

- smaller **cmc**
- lower γ_{cmc}
- ↑ Kp

⇓⇓

Excellent properties

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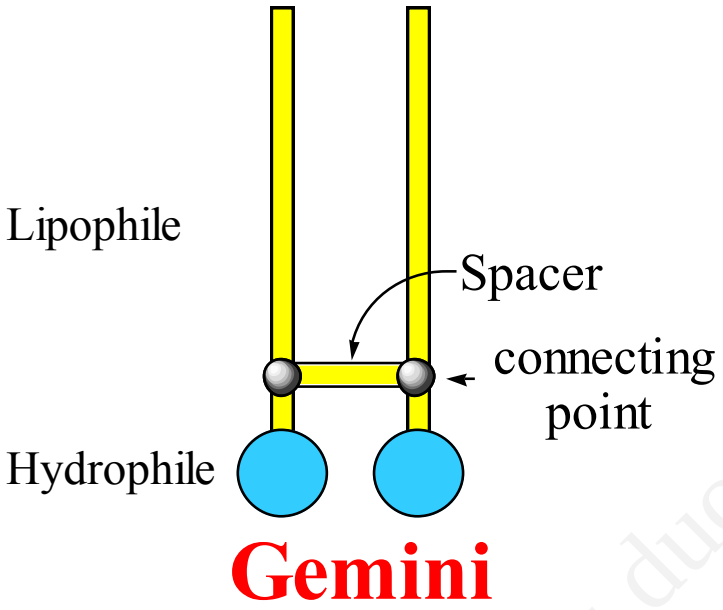
Structural Factor of Gemini



- Alkyl chain length (Lipophilicity)
- Kind of hydrophile (Hydrophilicity)

- Symmetry
  (same or different length of 2 lipophiles)
- Stereochemistry at connecting point
  (syn- /anti- isomer, optical isomer)
- Spacer length
- Kind of spacer

⇩

Chemical Structure *vs.* Surface Properties

Relationship

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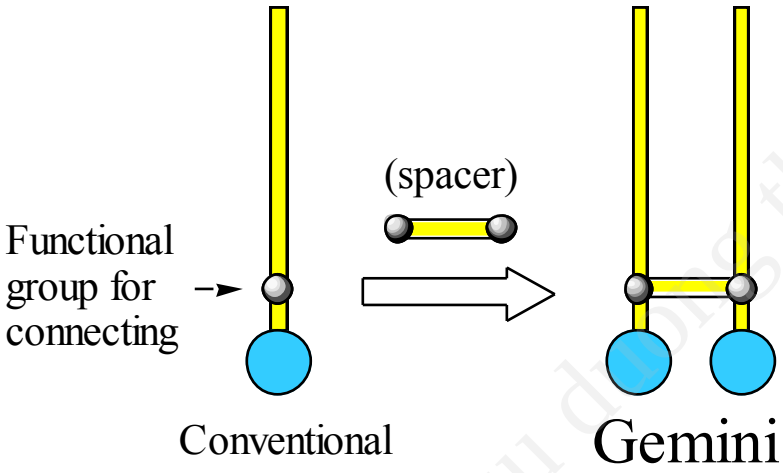
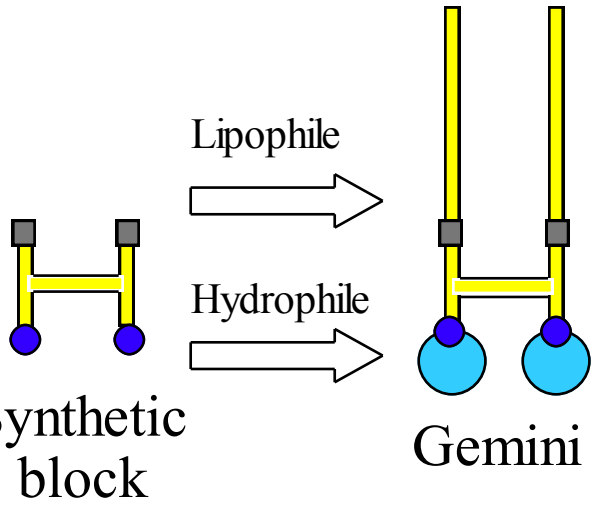
Synthetic Strategy of Gemini

Strategy 1; Connection of Conventional



- Malonic Gemini

Strategy 2; Synthetic Block



- Tartaric Gemini
- Gemsurf®

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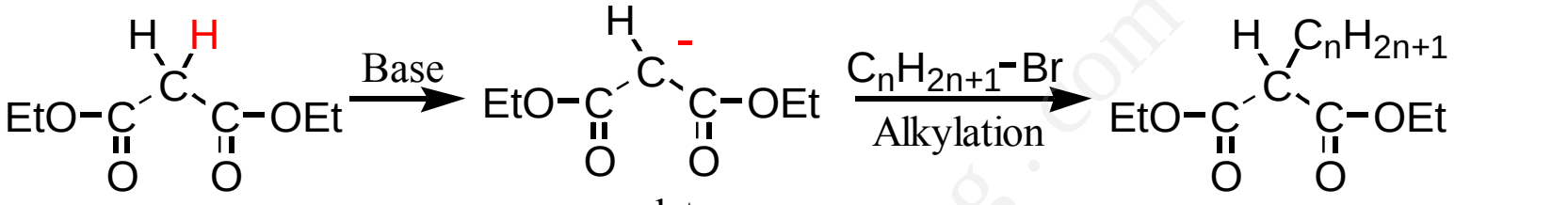
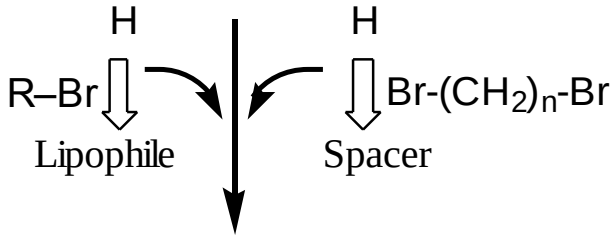
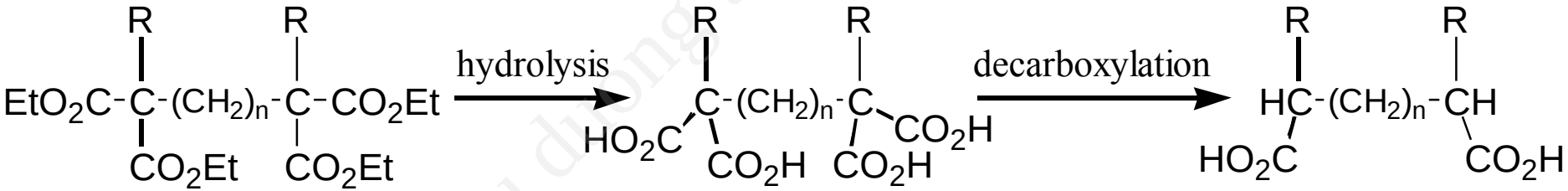
Synthetic Strategy for Malonic Gemini

Malonate





Malonic Gemini



2/4 Gemini

2/2 Gemini

feature

- No hetero atom at connecting point
- Several length of lipophile and space are available in large scale

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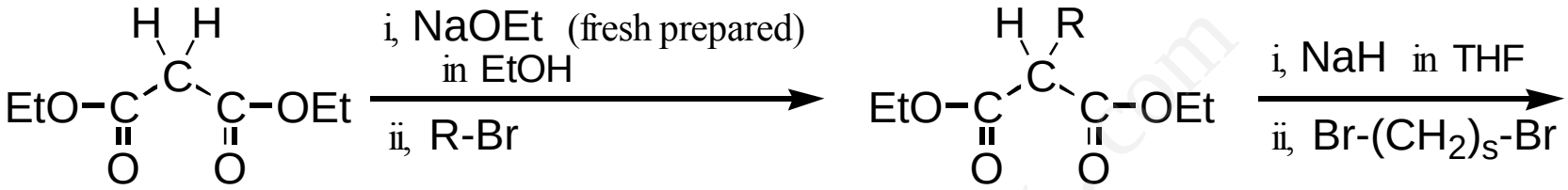
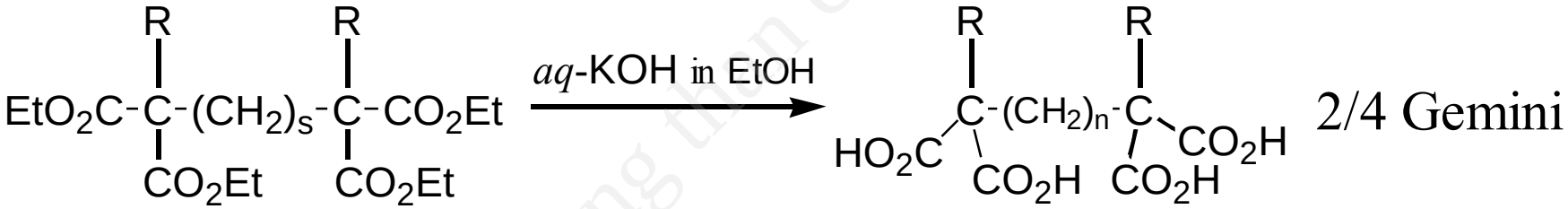
Preparetion of Malonic Gemini



Diethyl malonate

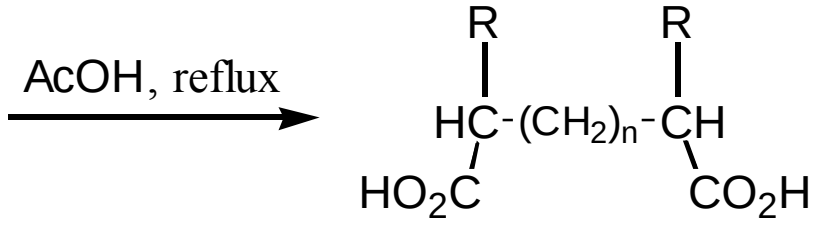
60-70 % yields



50-80 % yields

> 85 % yields

2/4 Gemini



65-95 % yields

2/2 Gemini

$R- = C_nH_{2n+1}-$

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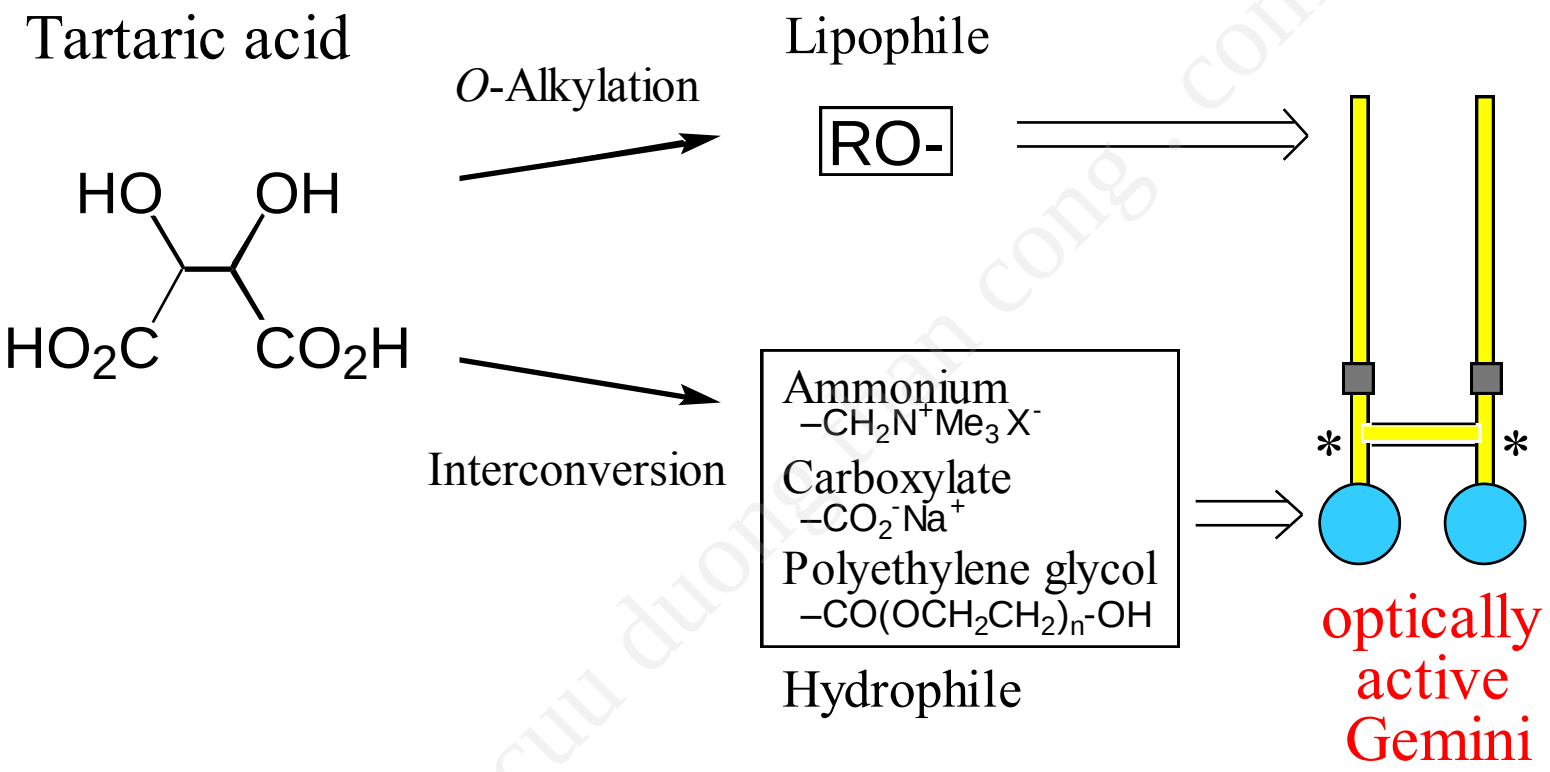
Synthetic Strategy for Tartaric Gemini



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feature

- L-, D-, and meso-Tartaric acid is commercially available.
- Cationic, anionic, and nonionic Gemini were prepared.

R- = C_nH_{2n+1}-

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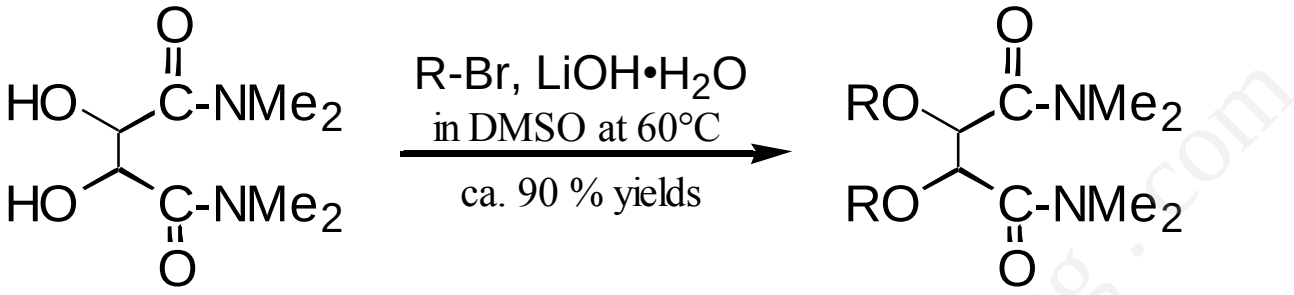
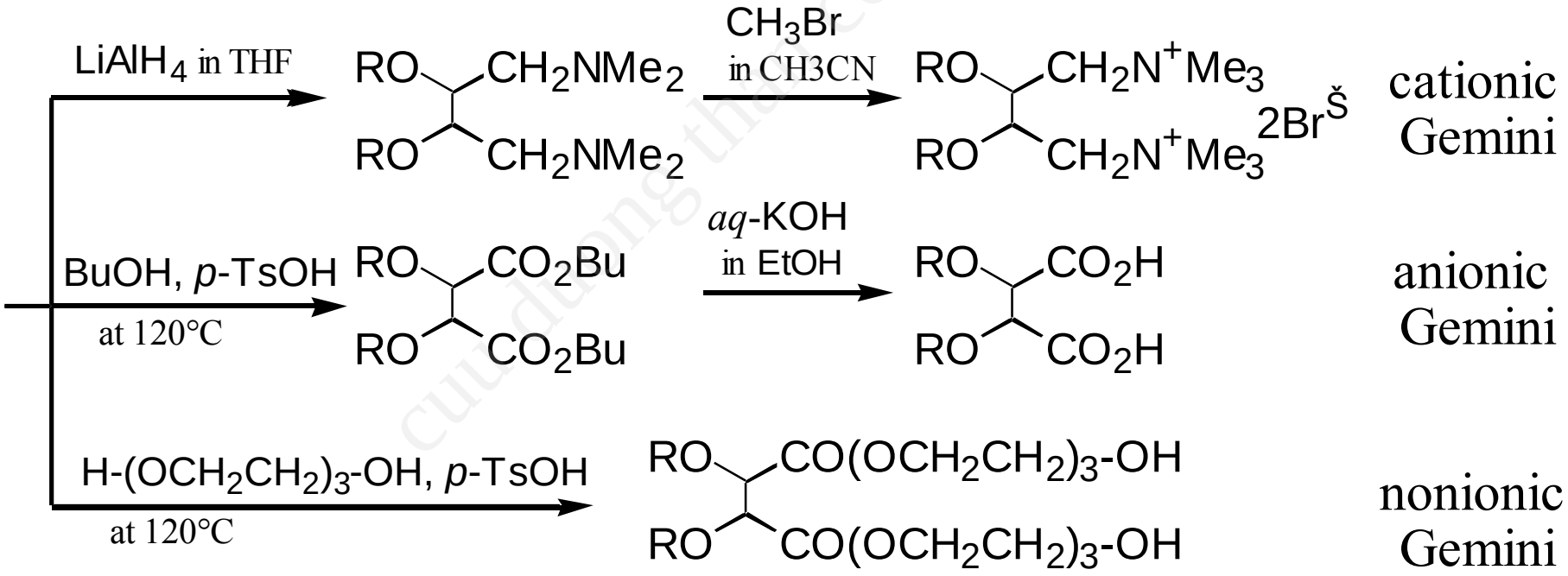
Preparetion of Tartaric Gemini



Tetramethyltartaramide



R- = C_nH_{2n+1}-

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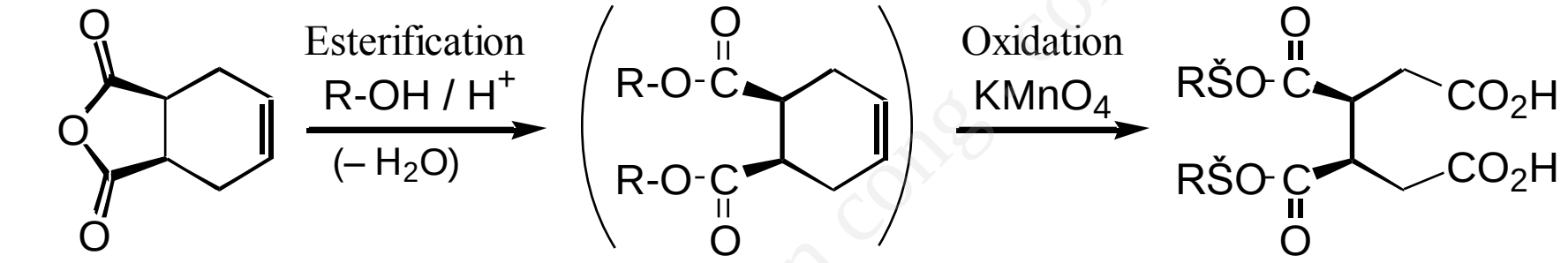
Synthetic Strategy for Gemsurf®



Tetrahydrophthalic anhydride

not isolated

Gemsurf®

>80% overall yield

R- = C_nH_{2n+1}-

feature

- 2 steps and one-pot synthesis
- Unexpensive starting materials and reagents

⇨ Large scale preparation → Commercially available Gemini

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Relationship between structure / surface properties

Significant factor

- Diastereo-isomerism : Big difference between meso- *vs.* dl- isomer
- Structural difference near connecting point

Less effective factor

- Optical-isomerism : Few difference between L- *vs.* D- isomer
- Equal length of 2 lipophile (symmetry)
  : Gemsurf with12+12, 14+10, and 16+8 alkyl chains
  are almost same properties
- Space length : small differences

⇩

Strong influence
of intramolecular lipophile interaction (hydrohobic)

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