Rule-based network analysis of complex reaction systems in biomass conversion

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Aditya Bhan
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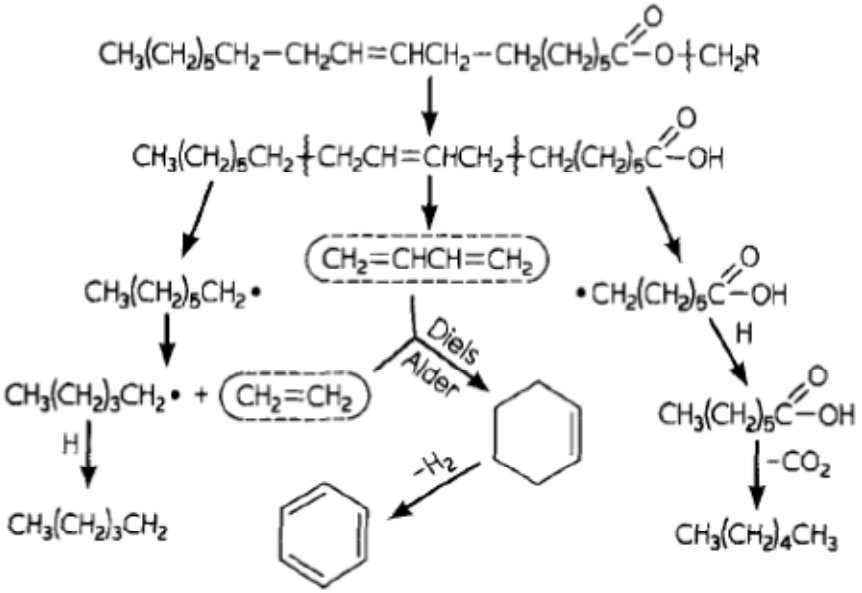
Session: Reaction Path Analysis II

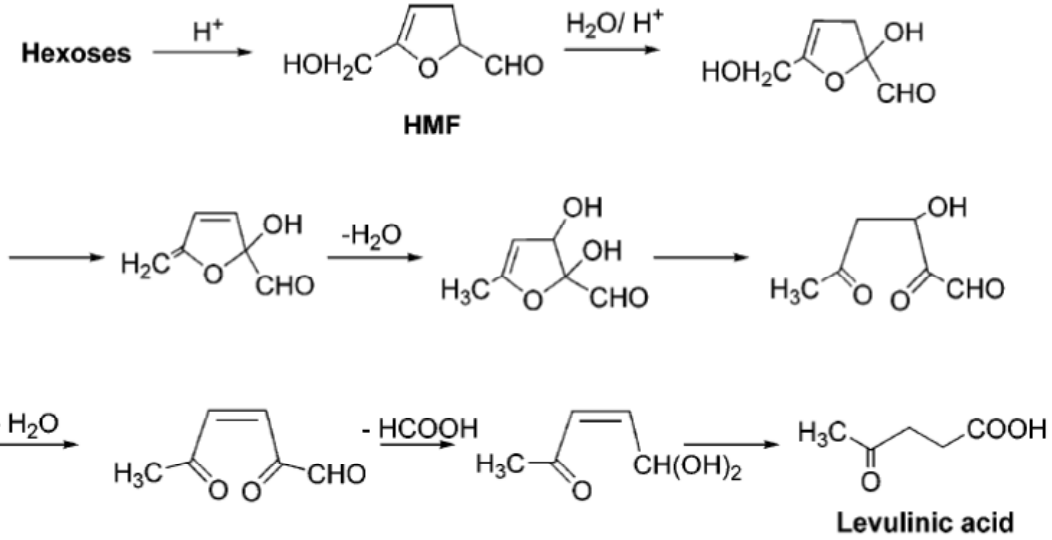
UNIVERSITY OF MINNESOTA

Complex reaction networks in biomass conversion



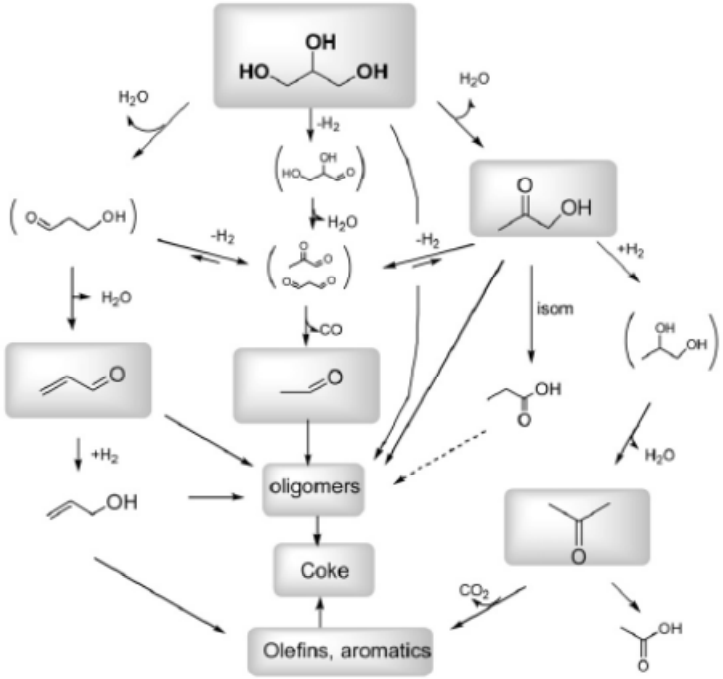
Pyrolysis of fatty esters (gas phase, free radical)

JAOCS, 1988, 65, 1781



Hexoses to Levulinic acid (homogenous, mineral acid catalyzed)

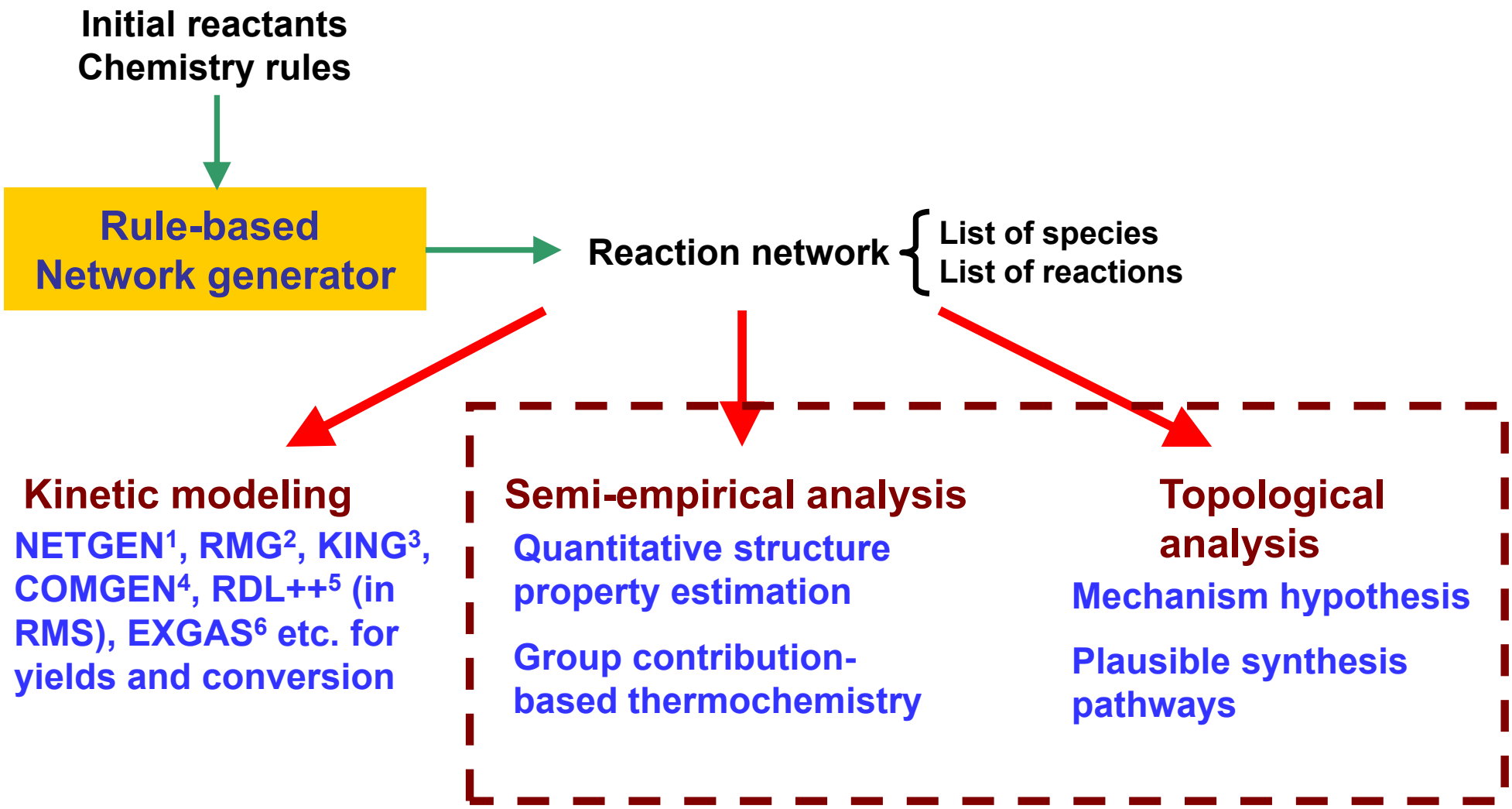
Chem. Rev. 2007, 107, 2411; Tetrahedron Lett. 1985, 26, 2111



Glycerol conversion on zeolites (heterogeneous, Bronsted acid catalyzed)

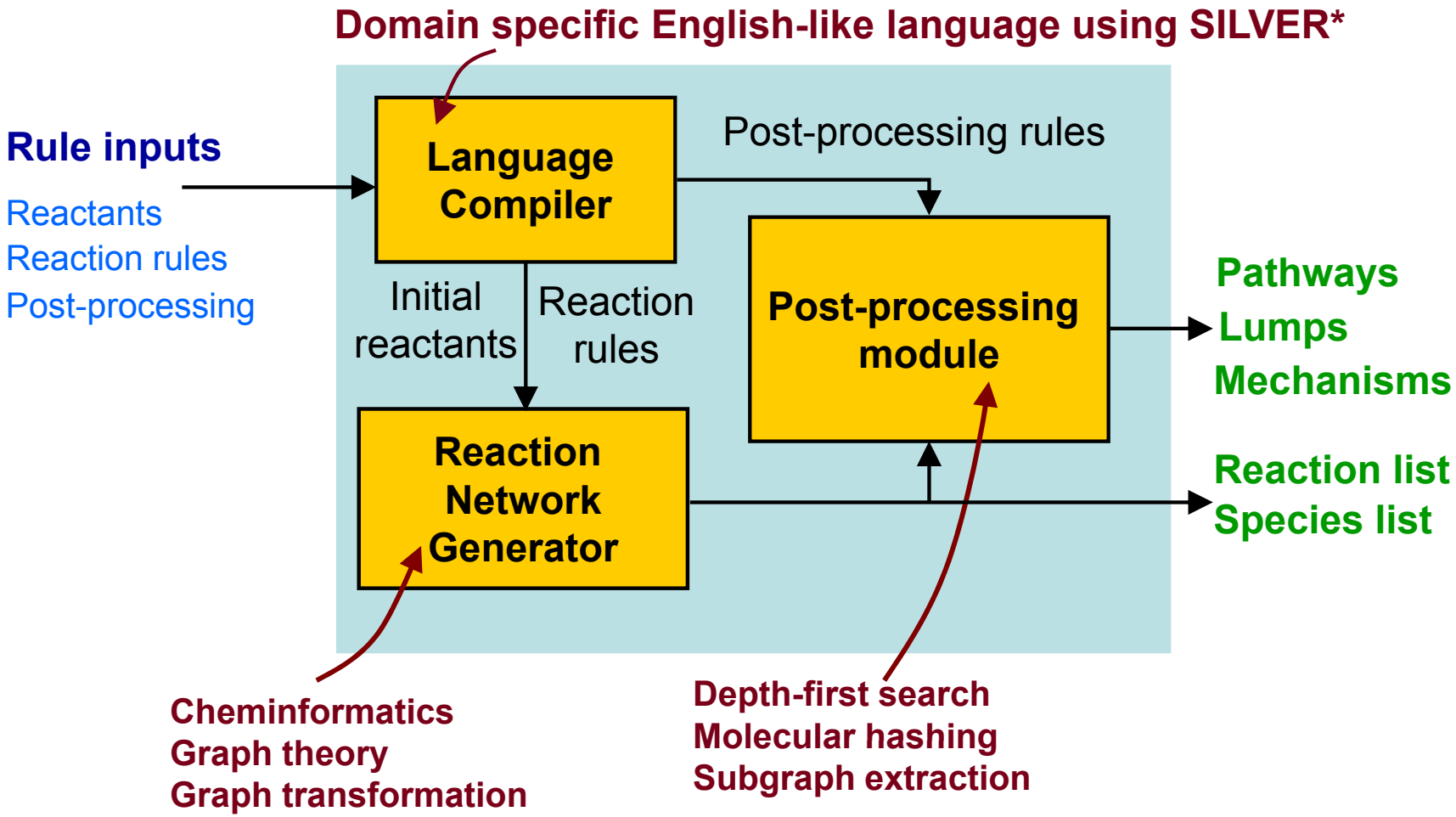
J. Catalysis 2008, 257, 163- 171

Network generation and three applications



[1] Ind.Eng.Chem.Res. 1994, 33, 790; [2] AIChE Journal 2006, 52, 718; [3] Chemical Engineering Science 1992, 47, 2713; [4] J.Chem.Inf.Model. 2003, 43, 36; [5] Comp. Chem.Eng. 2008, 32, 2455; 6 Combustion & Flame, 2001, 126, 1780

RING for network generation and analysis



*Developed by Eric Van Wyk group

Science of Computer Programming 2010, 75, 39

Ind.Eng.Chem.Res. 2010, 49 (21), 10459

RING Language Inputs & Reaction Network

Reaction rules

```
input reactant
"O1C(CO)(O)C(O)C(O)C1(CO)"
rule Protonation{
neutral reactant R1{
    C labeled c1 {connected to 2 C}
    O labeled o1 single bond to c1}
positive reactant R2{
    H+ labeled h1}
constraints{R1.size <15}
form bond (o1,h1)
modify atomtype (o1,O+)
modify atomtype (h1,H) }
```

REACTANT

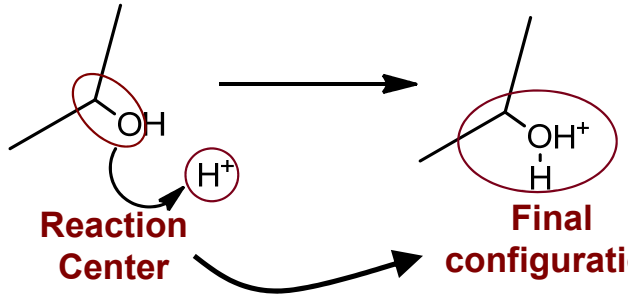
REACTION CENTER

CONSTRAINTS

TRANSFORMATIONS

Sample reactions: Fructose-HMF

SMILES string of Fructose



Graphical output of reactions using ChemDraw

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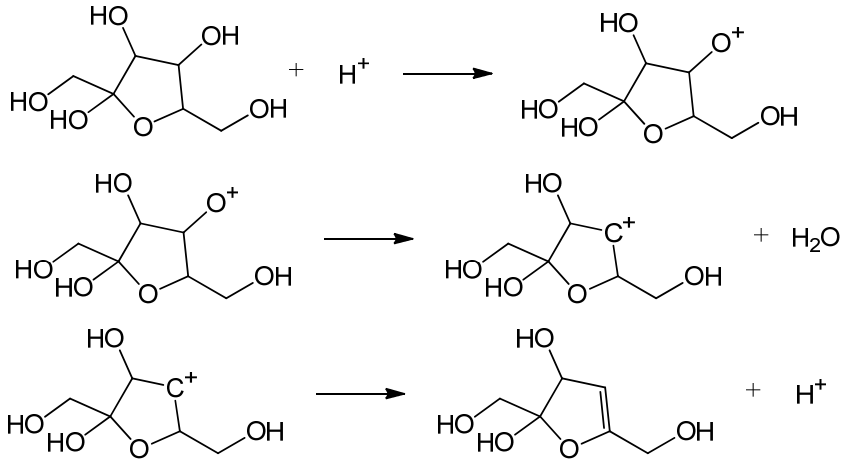
C1(C(C(C(CO)O1)O)O)(CO)O.[H+]>>C1(C(C(C(CO)O1)[O+])O)(CO)O
C1(C(C(C(CO)O1)[O+])O)(CO)O>>C1(C([C+]C(CO)O1)O)(CO)O.O
C1(C([C+]C(CO)O1)O)(CO)O>>C1(C(C=C(CO)O1)O)(CO)O.[H+]



Graphical output of reactions using ChemDraw

Reaction network size for different chemical systems

System	Species	Reactions
Fructose-to-HMF	546	1149
Propane aromatization	6943	4115463

RING Language Inputs & Reaction Network

Reaction rules

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"O1C(CO)(O)C(O)C(O)C1(CO)"
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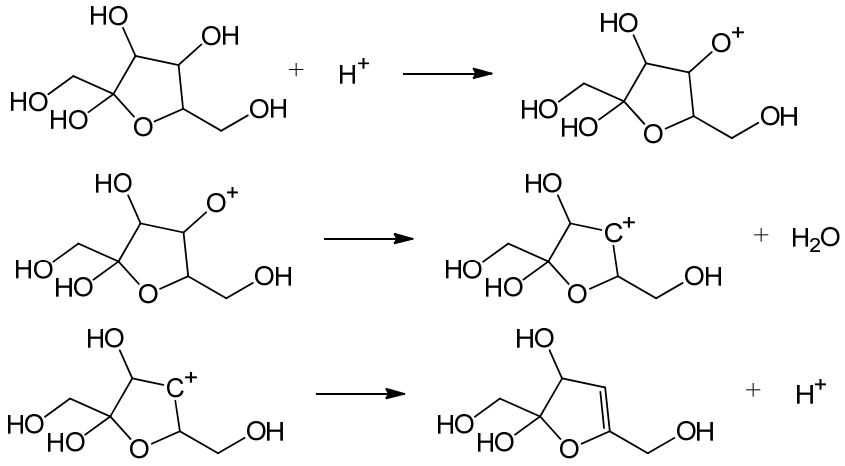
C1(C([C+]C(CO)O1)O)(CO)O>>C1(C(C=C(CO)O1)O)(CO)O.[H+]



Graphical output of reactions using ChemDraw

Pathways and Lumping instructions

```
// pathways instructions to HMF
Find pathways to mol{ mol is
"OCc1oc(C=O)cc1"} constraints{
   Length < 16
   contains <= 2 rule "HydrideShift"}
//Lumping rules for molecules
Lump all isomers {
   represent  acyclic with farthest
apart}
```

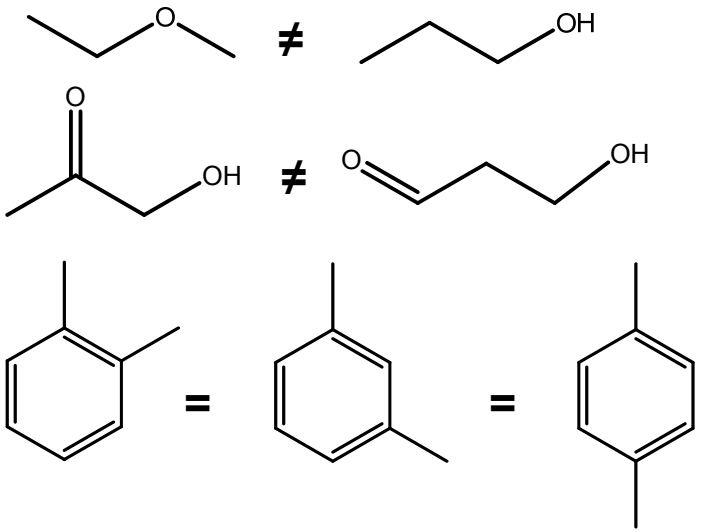
Pathways to HMF (Hydroxymethylfurfural)

Lumping instructions

Post-processing options with RING

Isomer Lumping

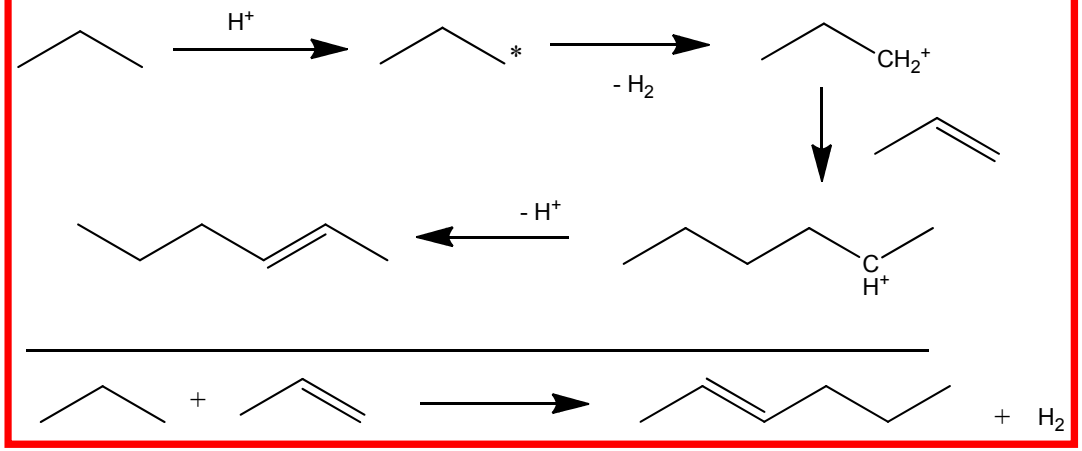
Functional equivalence



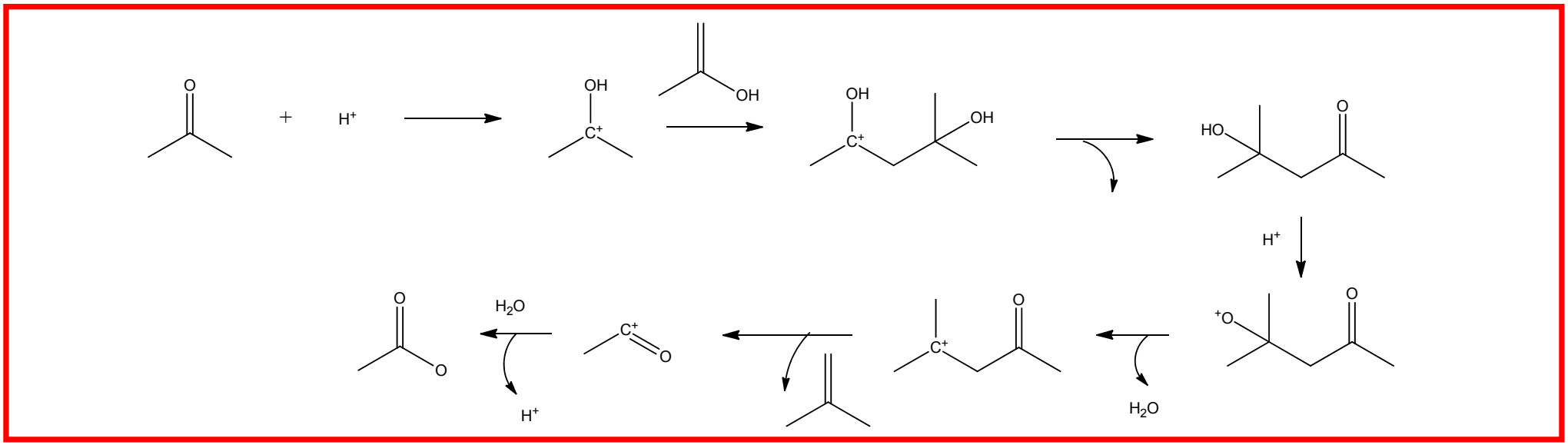
Mechanism enumeration

$C_3H_8 + C_3H_6 \rightarrow C_6H_{12} + H_2$

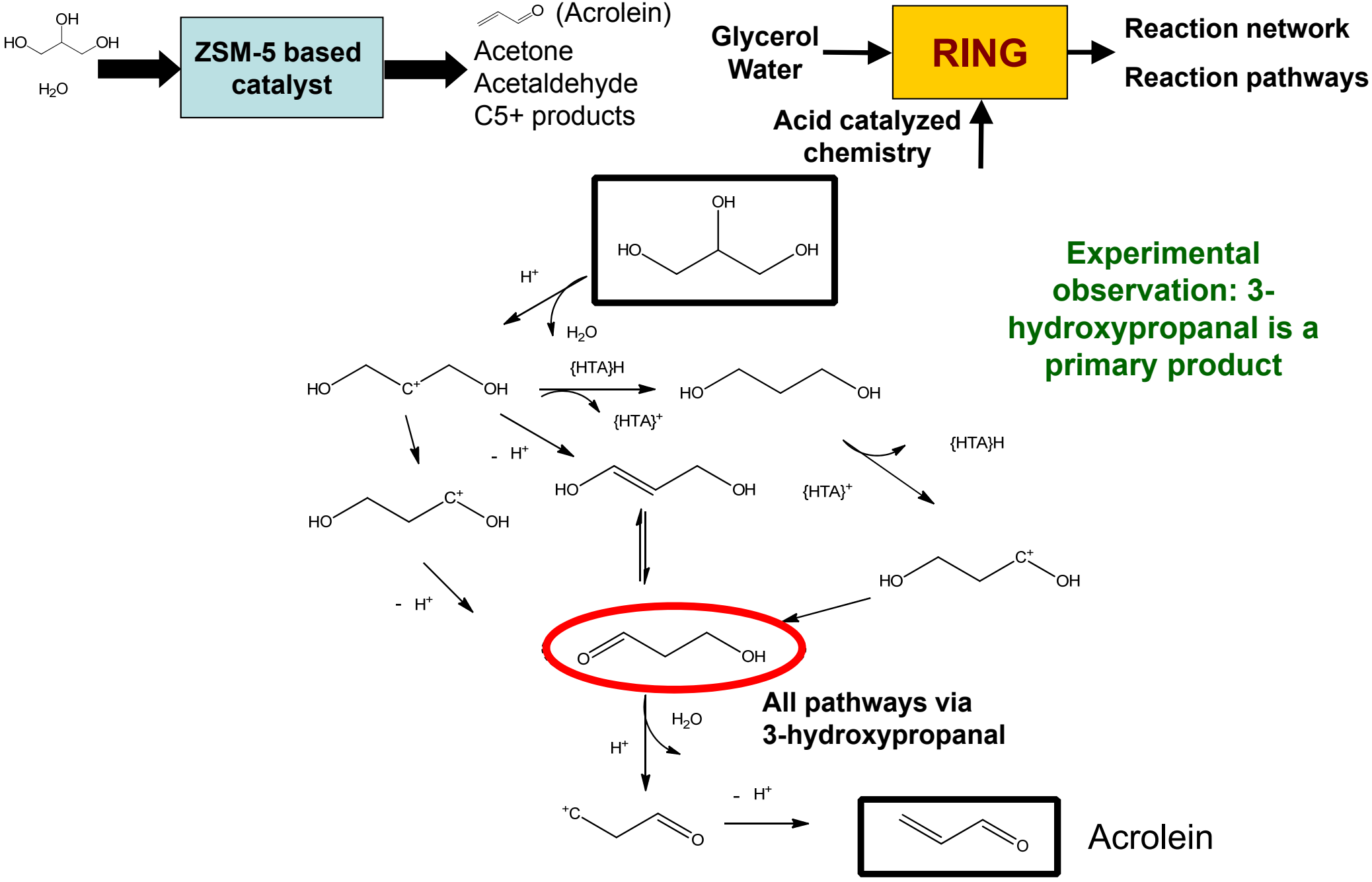
```
C(C)C.[H+]>>C([C*])C
C([C*])C>>C(C)[C+].[HH]
C(C)[C+].C(=C)C>>C([C+]C)CCC
C([C+]C)CCC>>C(=CCCC)C.[H+]
```



Pathways Identification



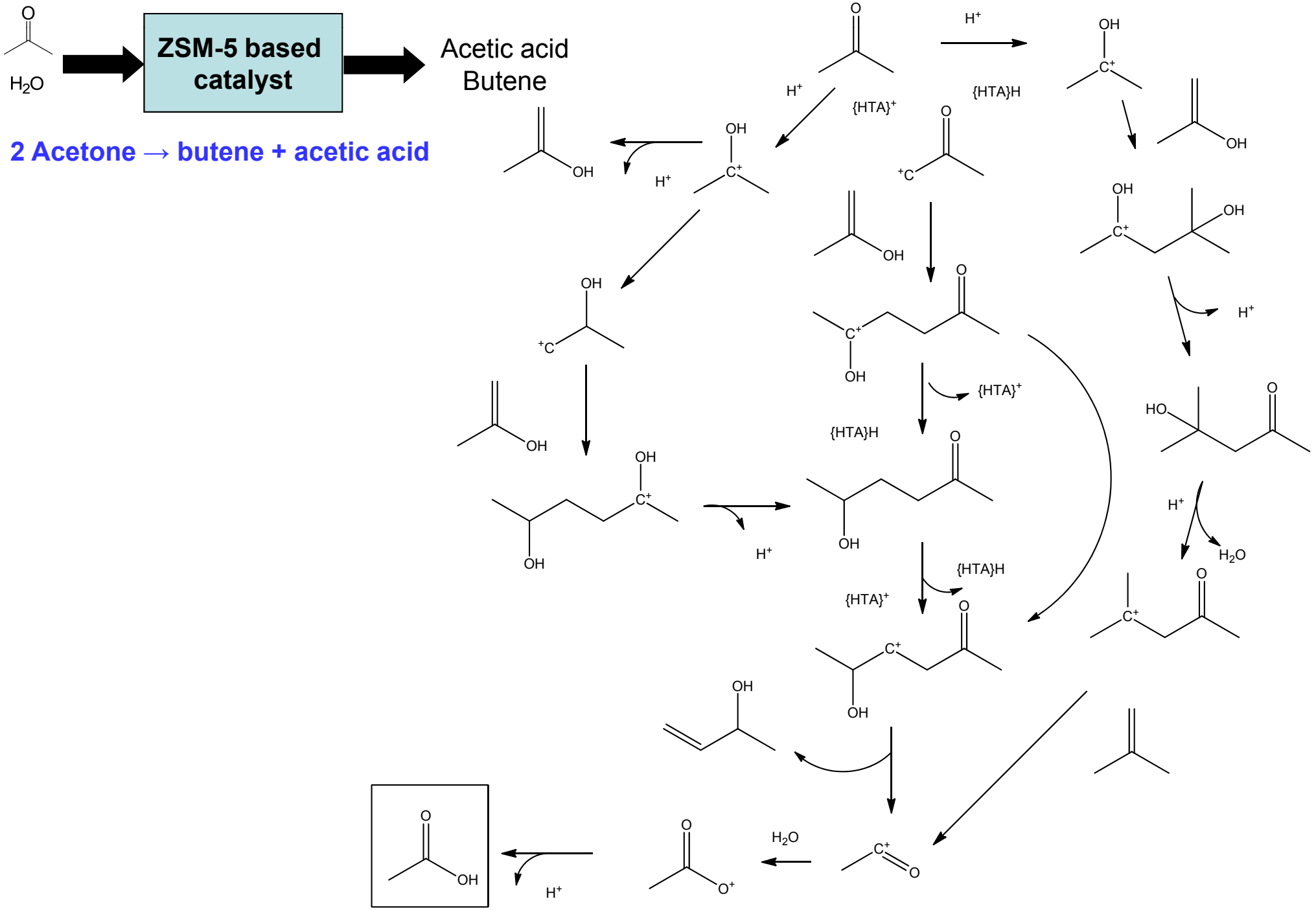
Mechanism hypothesis in complex systems



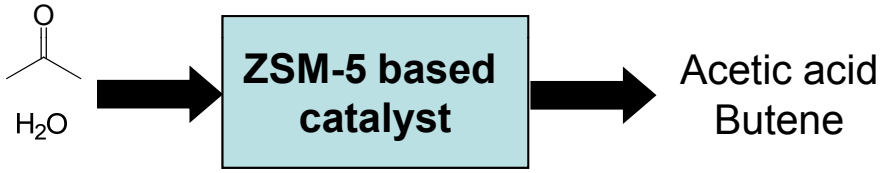
Experimental observation: 3-hydroxypropanal is a primary product

Journal of Catalysis 2008, 257 (1), 163

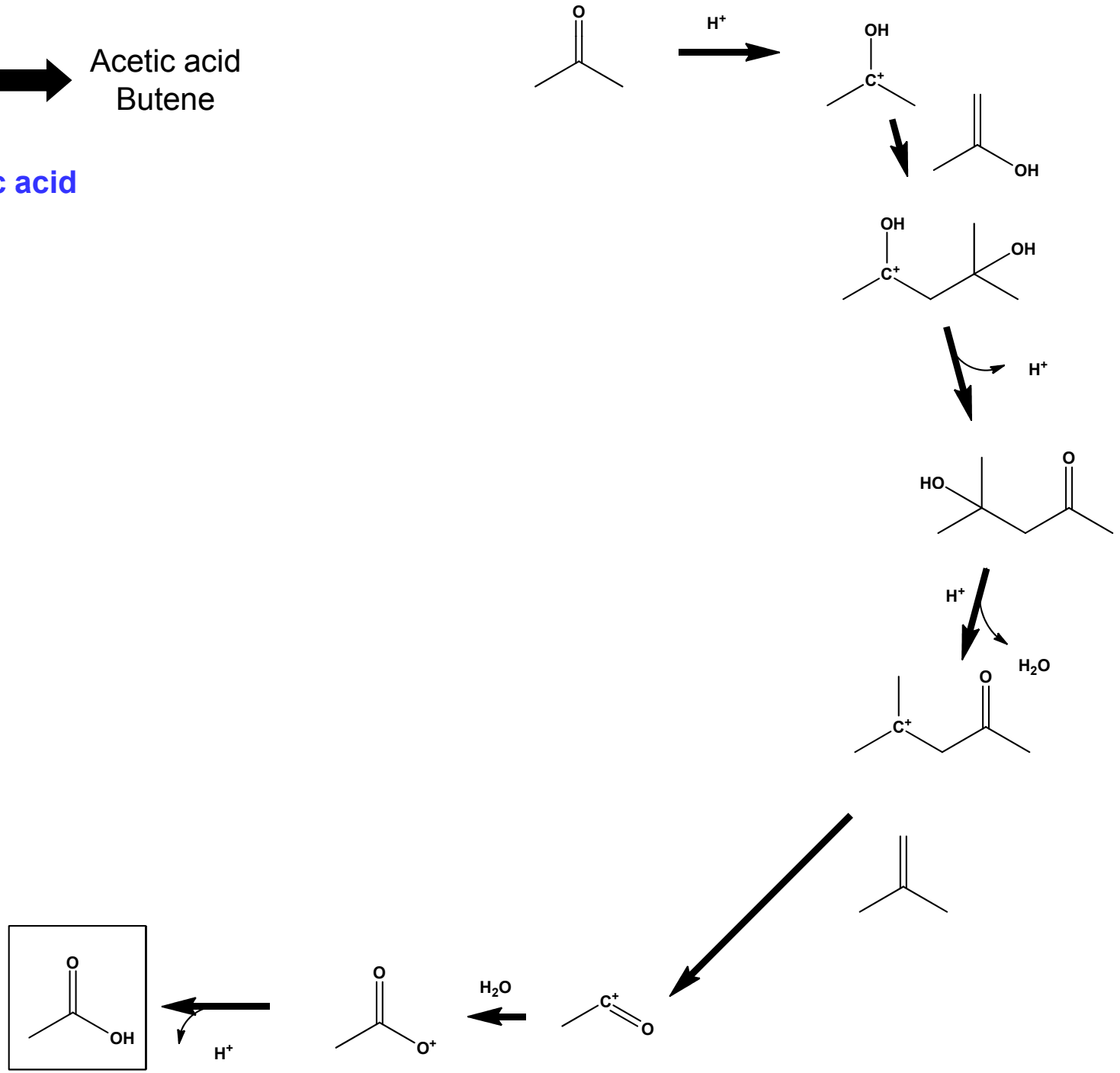
Mechanism of related system: Acetone conversion



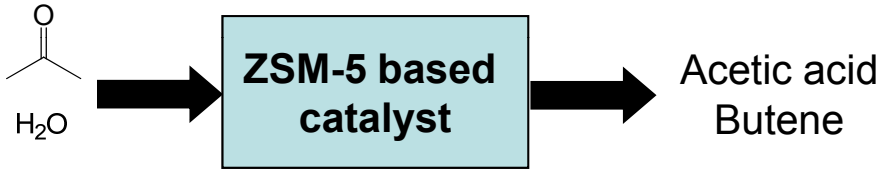
Mechanism of related system: Acetone conversion



2 Acetone → butene + acetic acid



Proposing possible experiments: isotope labeling



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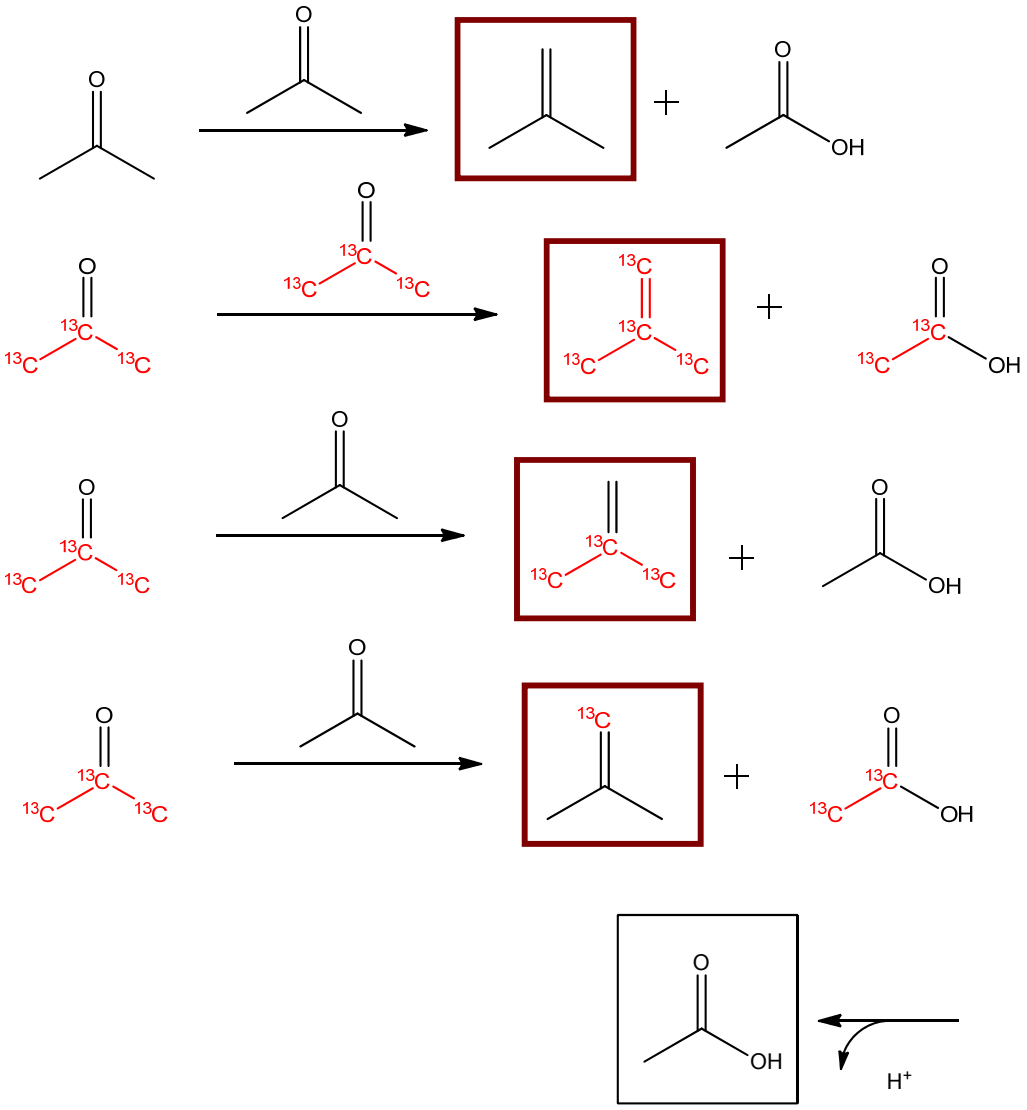
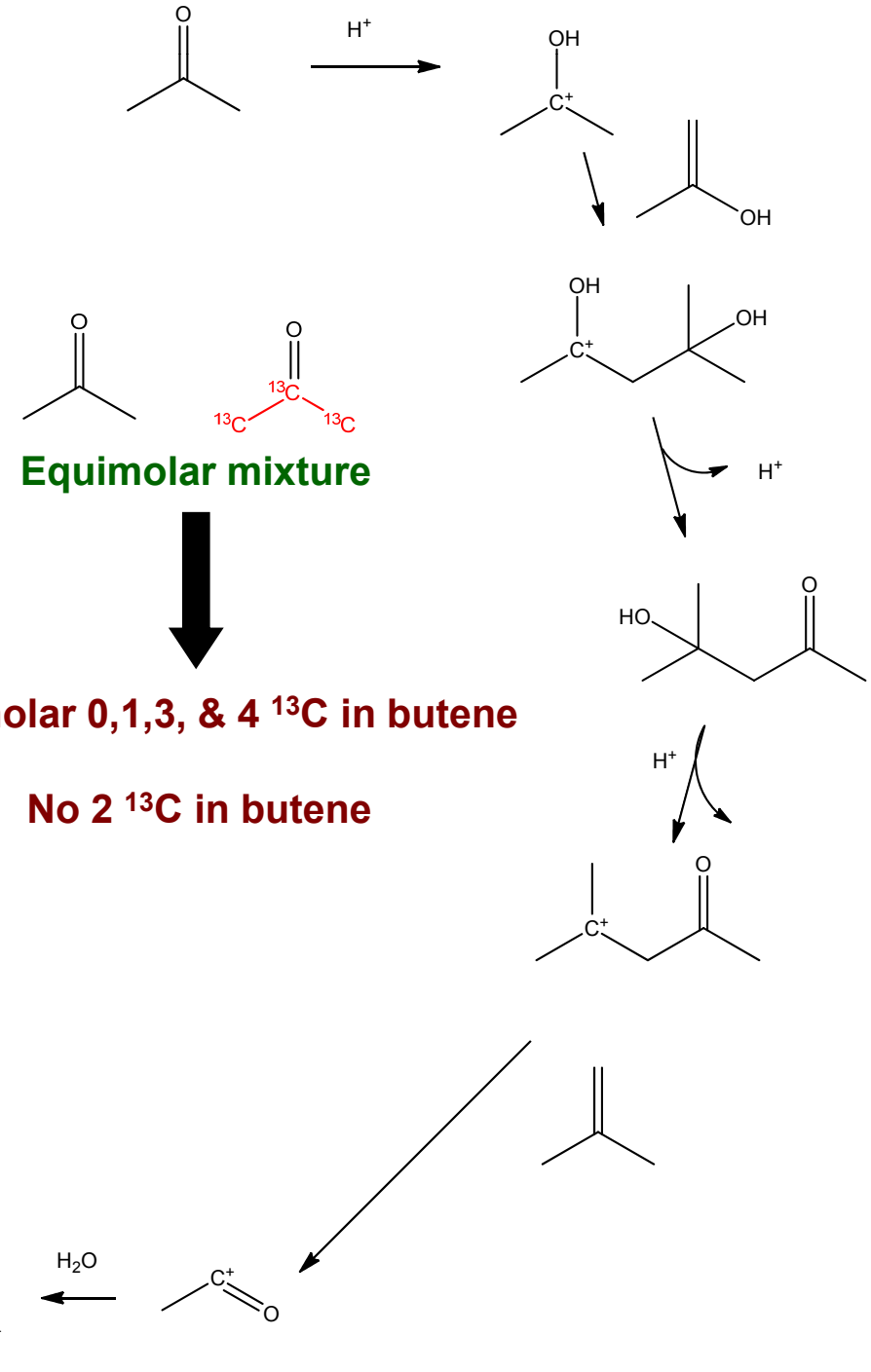


Equimolar mixture

Equimolar 0,1,3, & 4 ^{13}C in butene

No 2 ^{13}C in butene

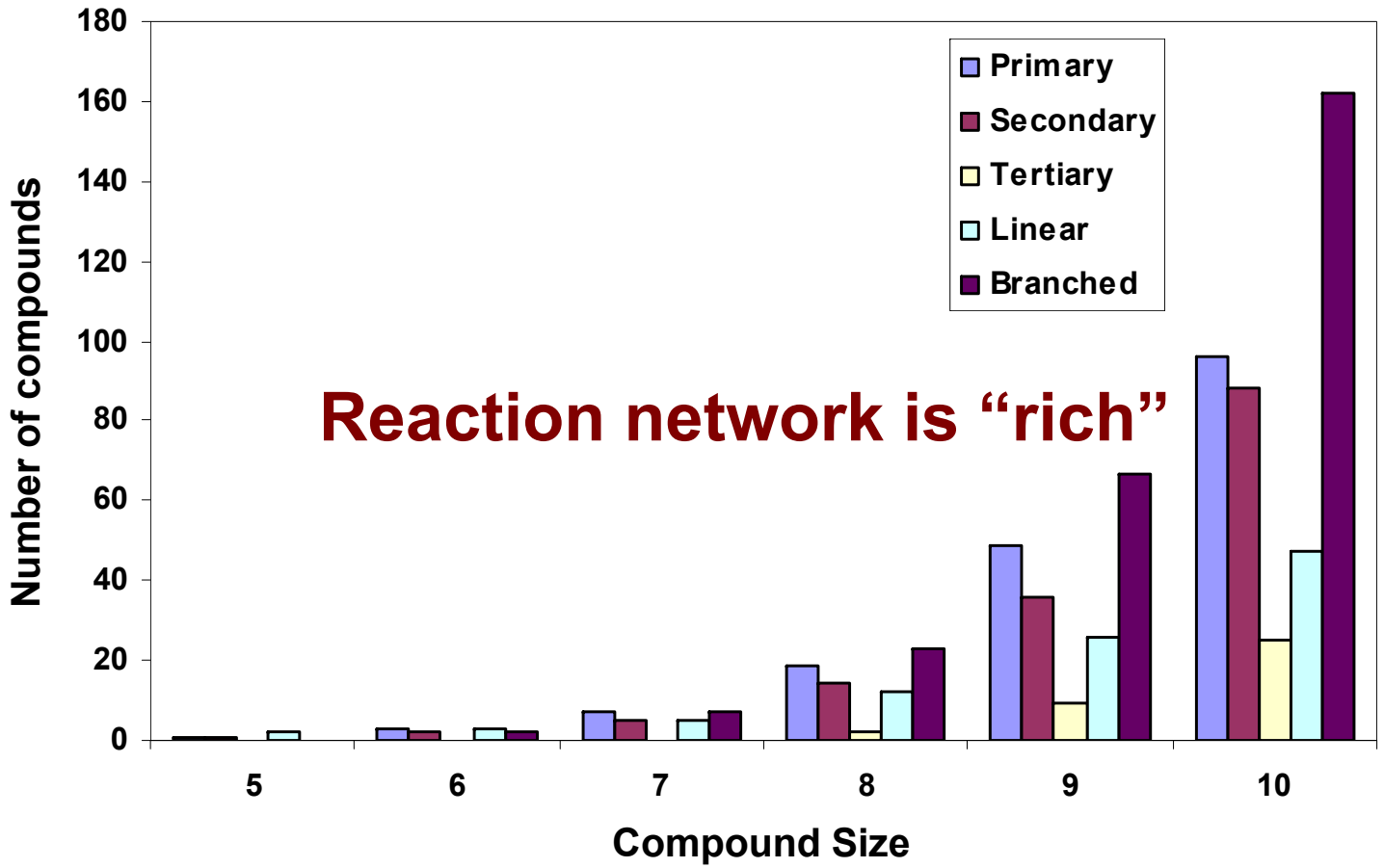


Identification of synthetic routes

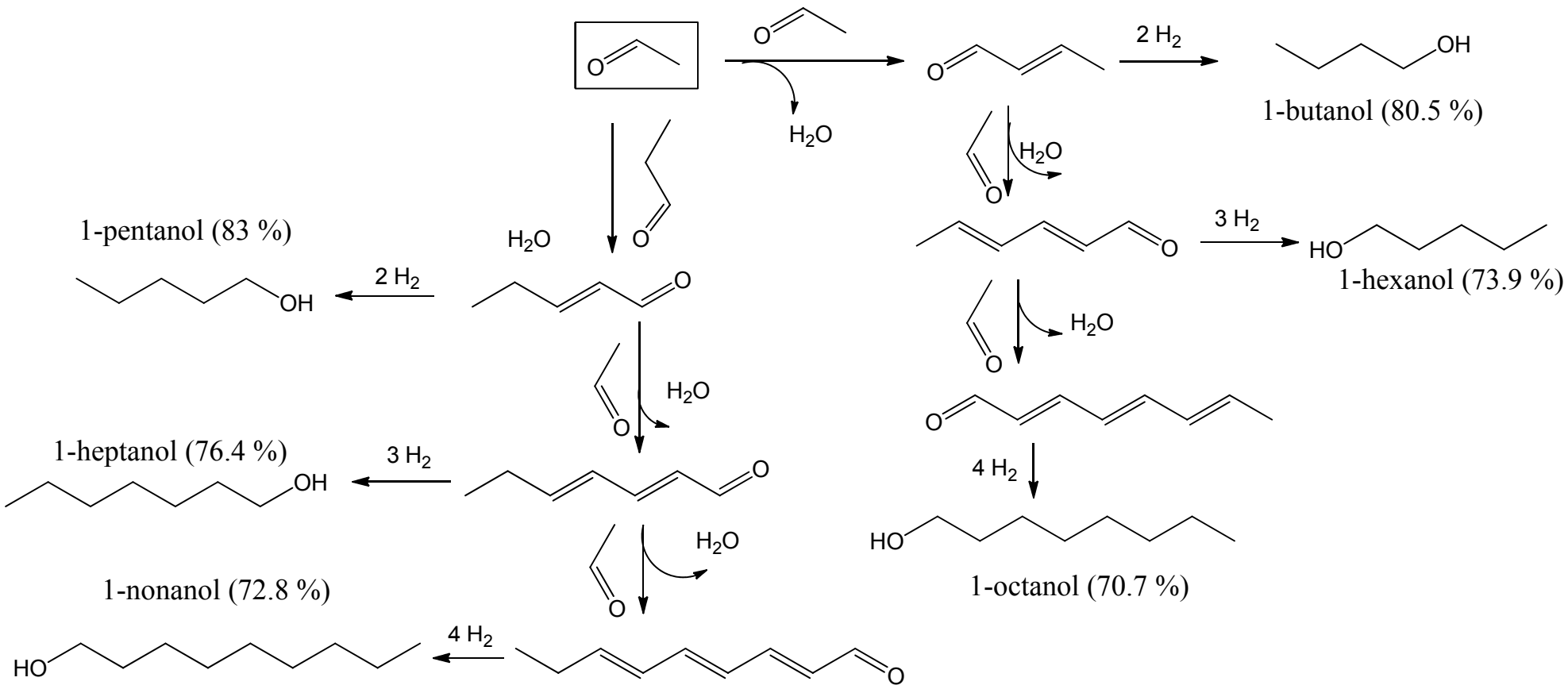
Synthesis pathways to alcohols from small oxygenates

Reactants: C2- and C3- acids, aldehydes, ketones, and alcohols

Chemistries: acid-catalyzed (dehydration, oligomerization, esterification), base-catalyzed (aldol condensation, ketonization), and metal catalyzed (hydrogenation/ dehydrogenation)



Querying most atom-efficient way to synthesize C_4-C_9 linear primary mono-alcohols



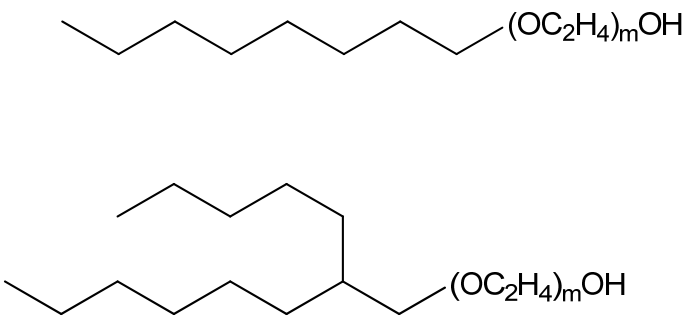
Nonionic surfactants: property estimation

Alkyl ethoxylates nonionic surfactants

$$C_nH_{2n+1}OH + mC_2H_4O \longrightarrow \boxed{C_nH_{2n+1}(C_2H_4O)_mOH}$$

Alcohol determines the hydrophobic part

Examples[1, 2]:



Desired physical properties of nonionic surfactants

- **Low Critical micelle concentration (CMC)**
- **High cloud point (CP)**

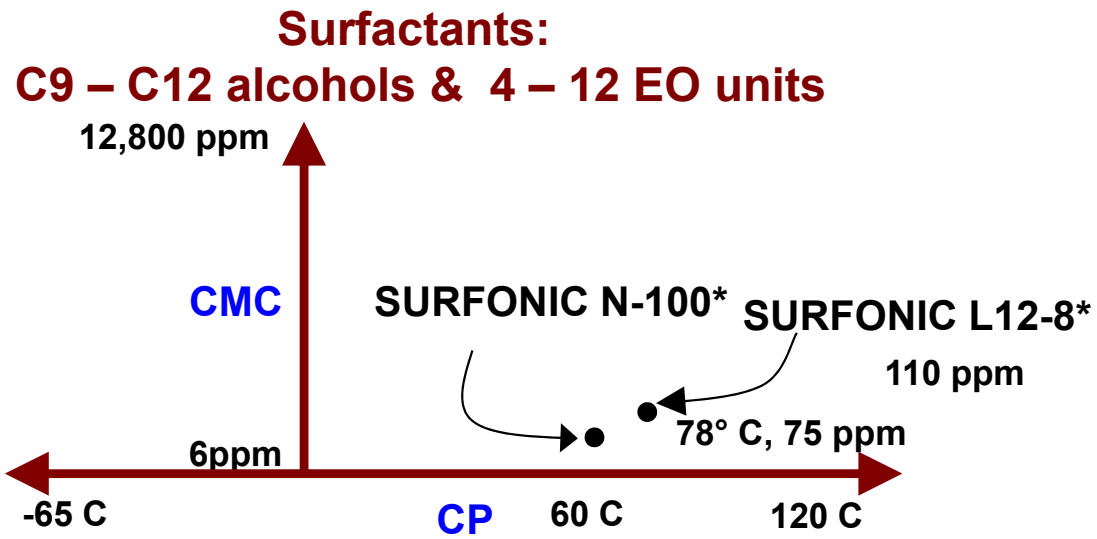
Synthesis problem: Find synthetically feasible alcohols that will lead to a surfactant with low CMC and high CP.

Quantitative structure-property relationships for nonionic surfactants

- **Critical Micelle concentration[1] & Cloud point[2]**
  - **Hydrophobic part – topological indices for size, shape and branching**
  - **Hydrophilic part – number of EO units / oxygen atoms**

[1] Langmuir 1996, 12, 1462 – 1470 [2] Journal of Colloid & Interface Science 1997, 193, 132 – 136

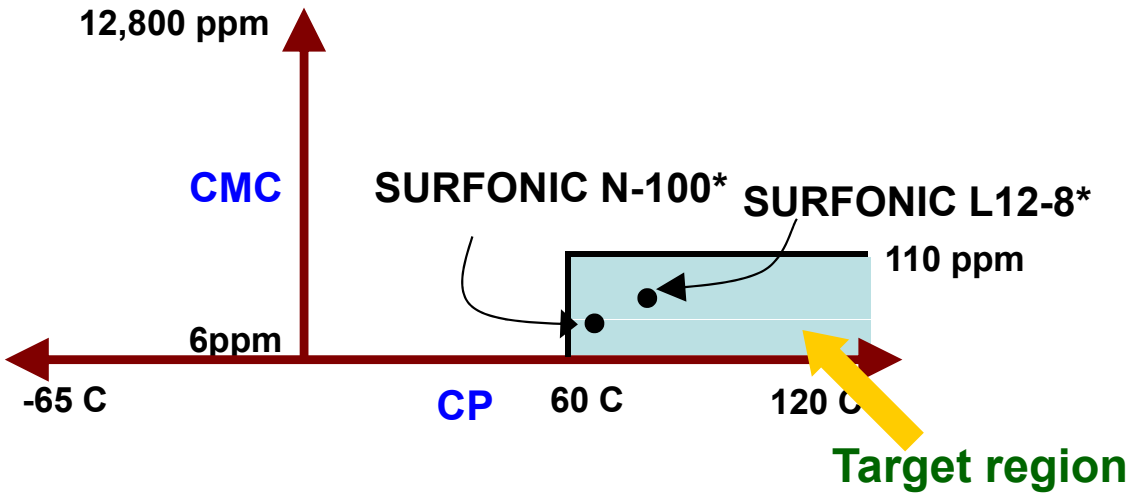
QSPR-based identification of alcohol ethoxylates

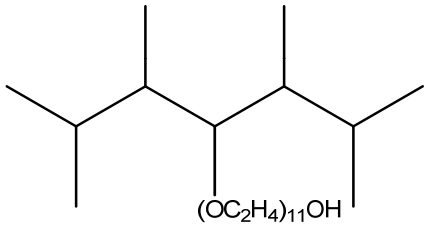


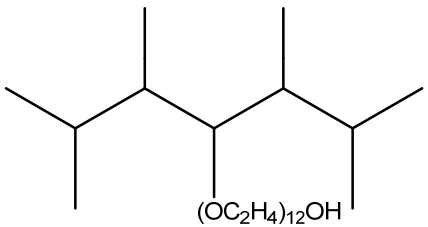
*http://www.huntsman.com/performance_products/

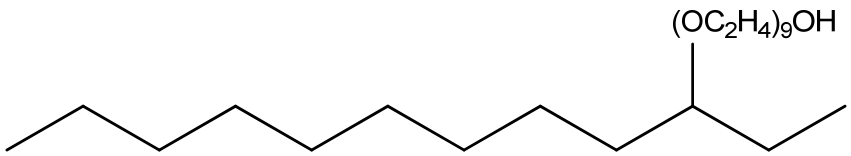
QSPR-based identification of alcohol ethoxylates

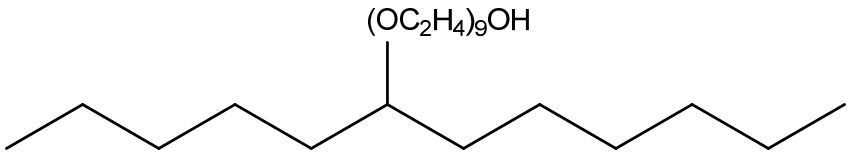
Surfactants:
C9 – C12 alcohols & 4 – 12 EO units

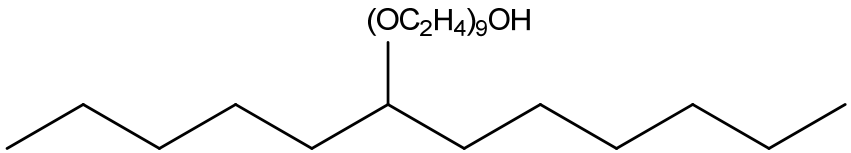


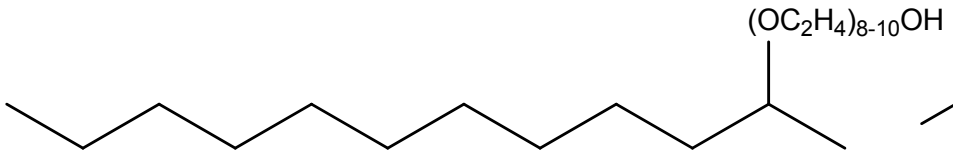


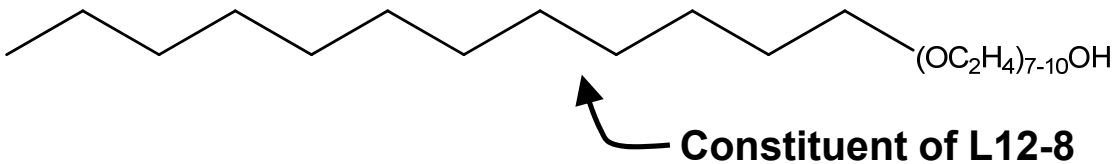












Constituent of L12-8

CMC: 56.4 – 110.3 ppm
CP: 60.5 – 107° C
HLB: 13 – 14.5

Water soluble
o/w Emulsifier

*http://www.huntsman.com/performance_products/

Summary

```
Reactant is
"O1C(CO)(O)C(O)C(O)C1(CO)"

Rule Protonation{
Neutral reactant R1{
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   R1 is cyclic}
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Modify atomtype (o1,O+)
Modify atomtype (h1,H)}
```
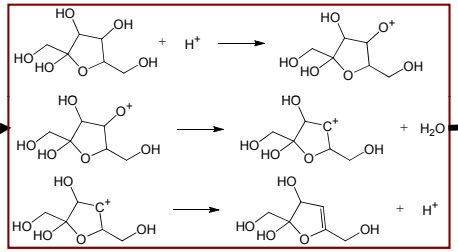

Input code

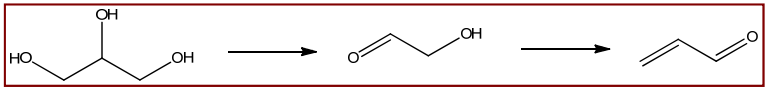
RING



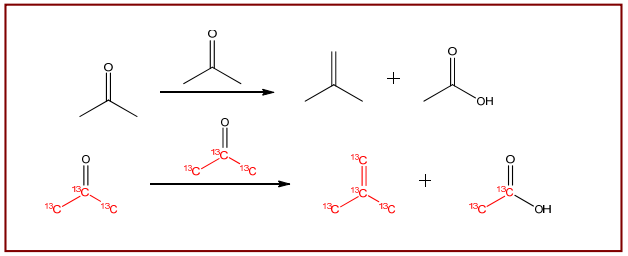
Reaction network

Post-processing (lumps, mechanisms, and pathways)

Mechanism Hypothesis through pathway analysis



Glycerol dehydration

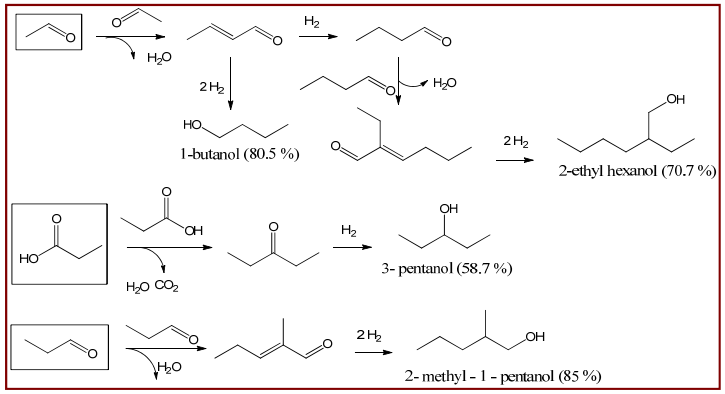


Acetone conversion mechanism

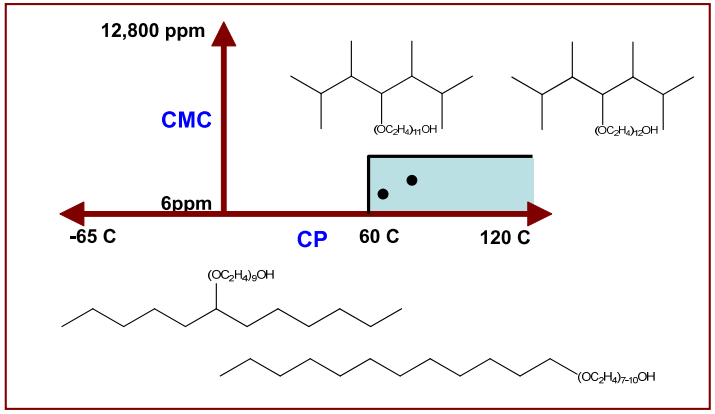
Synthetic pathways through mechanism analysis

+

QSPR based product property correlations



Synthetic pathways to alcohols



QSPR-based identification of products

RING is available upon request

Acknowledgements

- Eric Van Wyk group (Univ of Minnesota)
- Catalysis Center for Energy Innovation (US – DOE)
- NSF EFRI, IREE - UMN