Demonstration of RING

Udit Gupta and Dion Vlachos

Complex reaction networks are ubiquitous

Chemistry	System	Reactions (species)
Heterogeneous catalysis	Propane aromatization	19907 (5909)
Gas phase combustion	Hexadecane combustion[1]	8130 (2116)
Metabolism	E.coli genome[2]	2077 (1039)
Metal chemistry	Glycerol decomposition[3]	3313 (537)

[1] Combustion and Flame 2009, 156 (1), 181; [2] Mol Syst Biol. 2007, 3, 121; [3]Green Chem., 2014,16, 813

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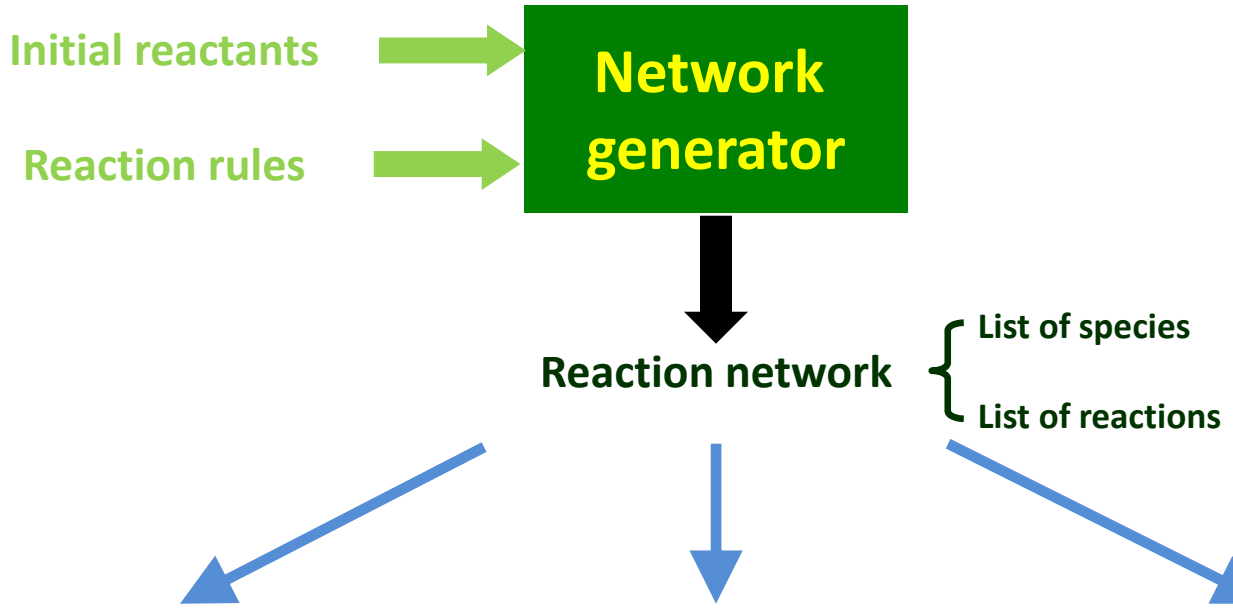
- Manual construction generally impractical
- Automated network generators
  - Generate all possible reactions and species of the network
  - Use reaction rules as basis – **"rule-based"**

[1] Combustion and Flame 2009, 156 (1), 181; [2] Mol Syst Biol. 2007, 3, 121; [3]Green Chem., 2014,16, 813

Reaction network generator can be used to construct the network



Kinetic modeling

Prediction of yield and conversion

NETGEN[1], RMG[2], KING[3], COMGEN[4], RDL++[5] (in RMS), EXGAS[6] etc.

Semi-empirical analysis

Direct computation (semi-empirical, ab initio, DFT)

Group contributions

Network analysis

Mechanism hypothesis

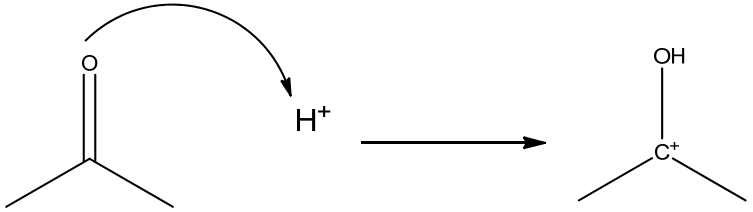
Feasible synthesis pathways

[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

Rule-based network generation:
Some basic definitions

Reaction rule

- Describes the fundamental transformation
- Elementary/ non-elementary steps



Rule: Protonation of a carbonyl group

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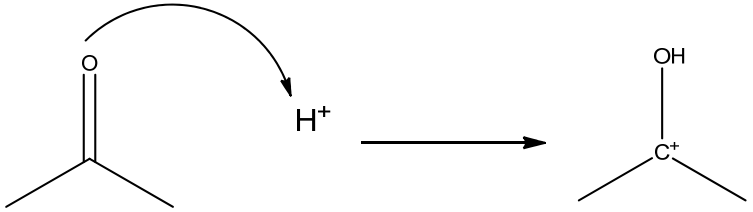
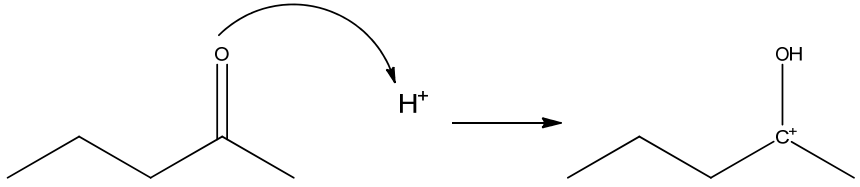


Rule: Protonation of a carbonyl group

Reaction

- An application of a rule on a reactant molecule
- One rule can lead to several reactions



Reaction: Protonation of a 2-pentanone

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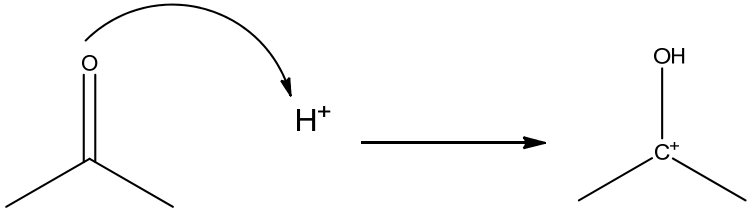

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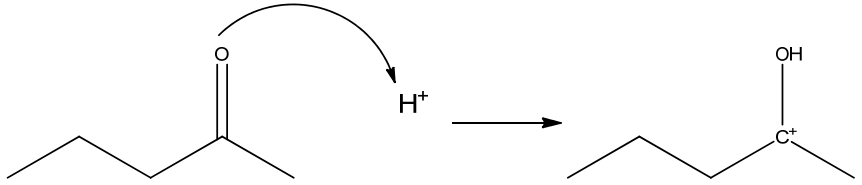
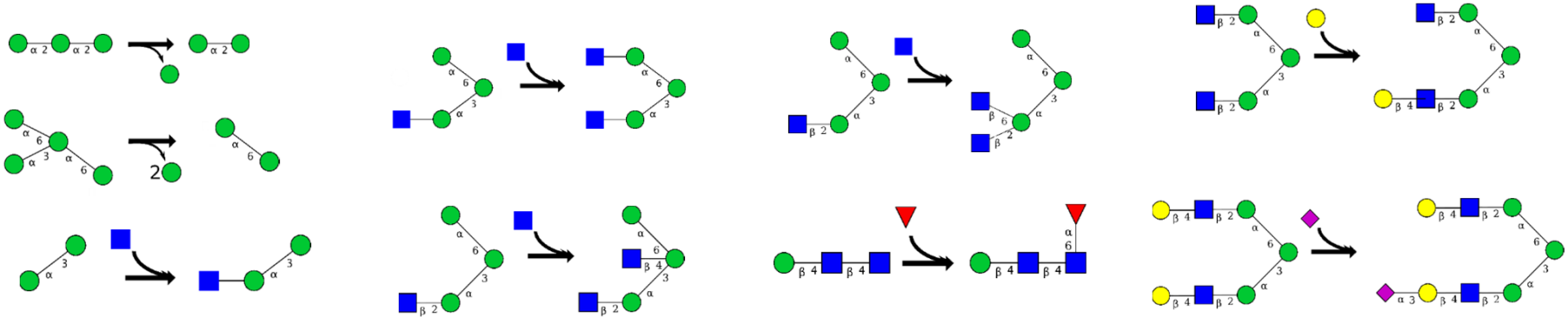


Reaction: Protonation of a 2-pentanone

Set of reaction rules (N-Glycosylation reaction network)



Examples of Reaction Rules for Acid Catalyzed Chemistry

Reaction families:

1. **Protonation of C=C**
2. Protonation of an alcoholic group of a cyclic molecule
3. Dehydration of oxonium species to form carbenium ion
4. Deprotonation of carbenium to form C=C
5. Deprotonation to form ketone
6. Hydride shifts
7. Allylic rearrangement

RING language: rule inputs

User-specification

```
input reactant "C=CC"
input reactant "[{Zeo}H] "
input reactant "N#N"

rule OlefinAdsorption{
gasPhase reactant r1{
   C labeled c1
   C labeled c2 double bond to c1}
reactant r2{
   Zeo labeled z1 {! connected to >=1 C with
    any bond}
    H labeled h1 single bond to z1}

constraints{! r1 is cyclic}

form bond (c1,z1)
decrease bond order (c1,c2)
form bond (c2,h1)
break bond (z1,h1) }
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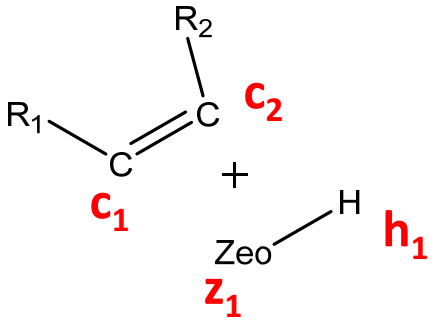
REACTION CENTER

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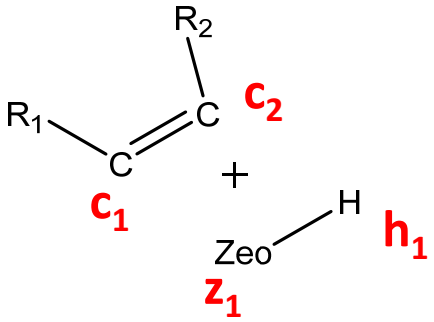

Reaction Center

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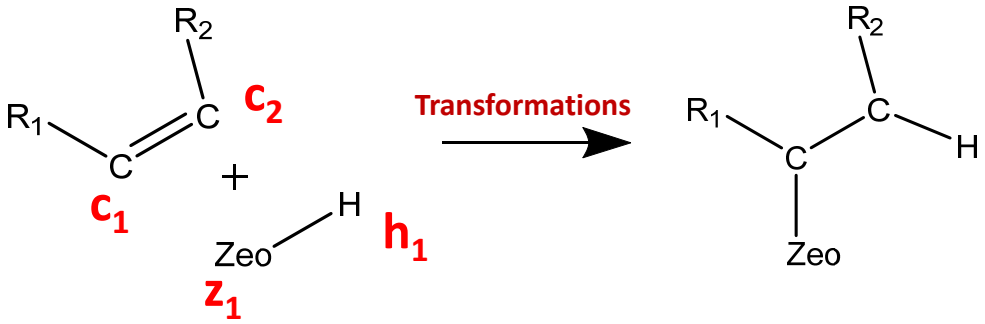

Reaction Center

Final configuration

```
constraints{! r1 is cyclic}
```

CONSTRAINTS

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form bond (c1,z1)
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```
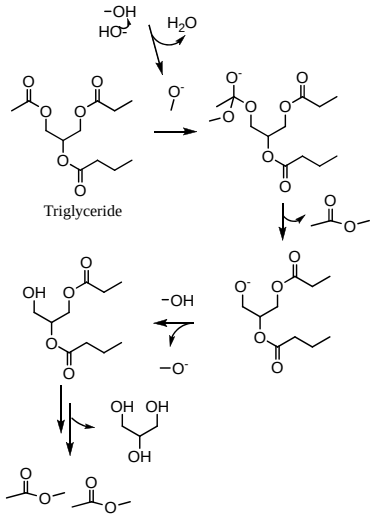
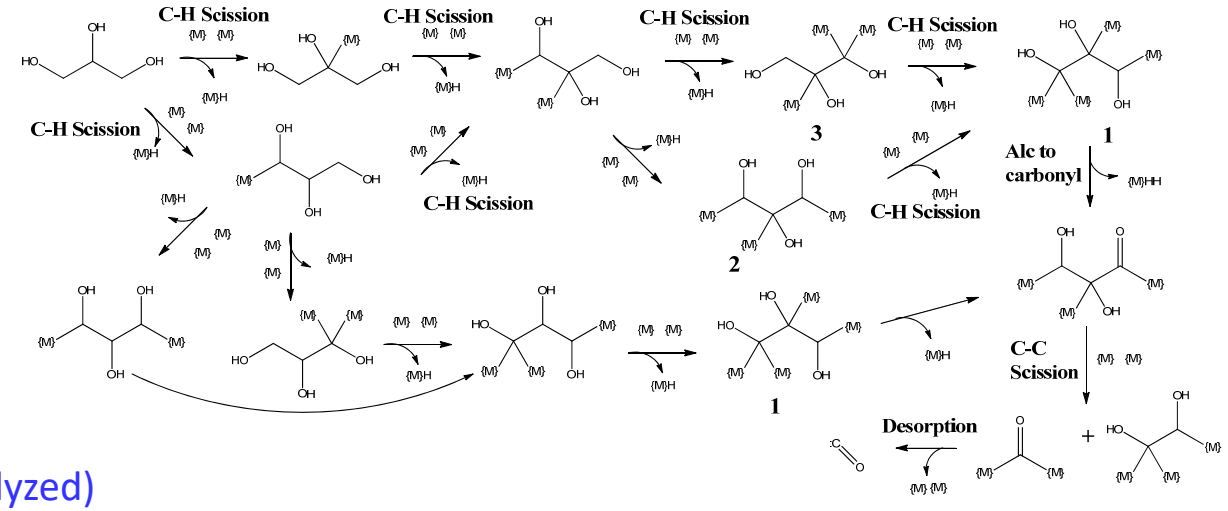

TRANSFORMATIONS

Diverse chemistries handled using RING

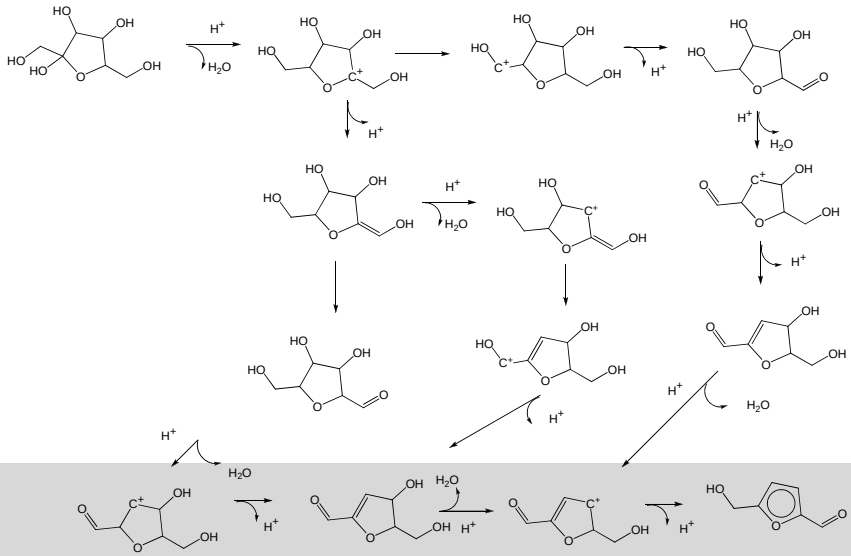
Transesterification (base cat.)



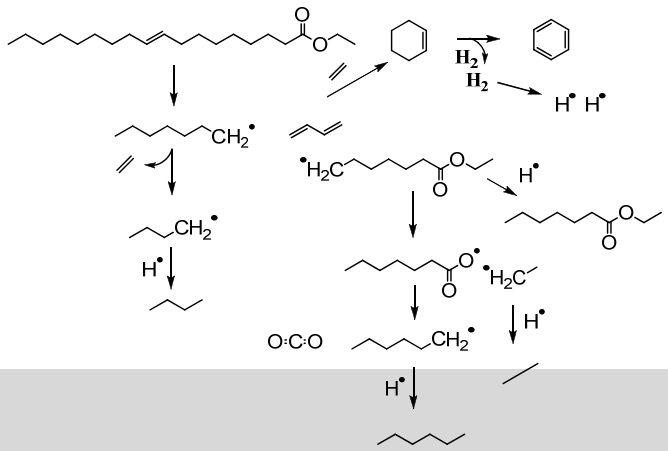
Glycerol decomposition (metal catalyzed)



Fructose-to-HMF (acid catalyzed)



Pyrolysis of fatty esters (free radical)



Additional Information

Weblinks:

- https://bhan.cems.umn.edu/software
- https://daoutidis.cems.umn.edu/software
- https://conservancy.umn.edu/handle/11299/197603

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