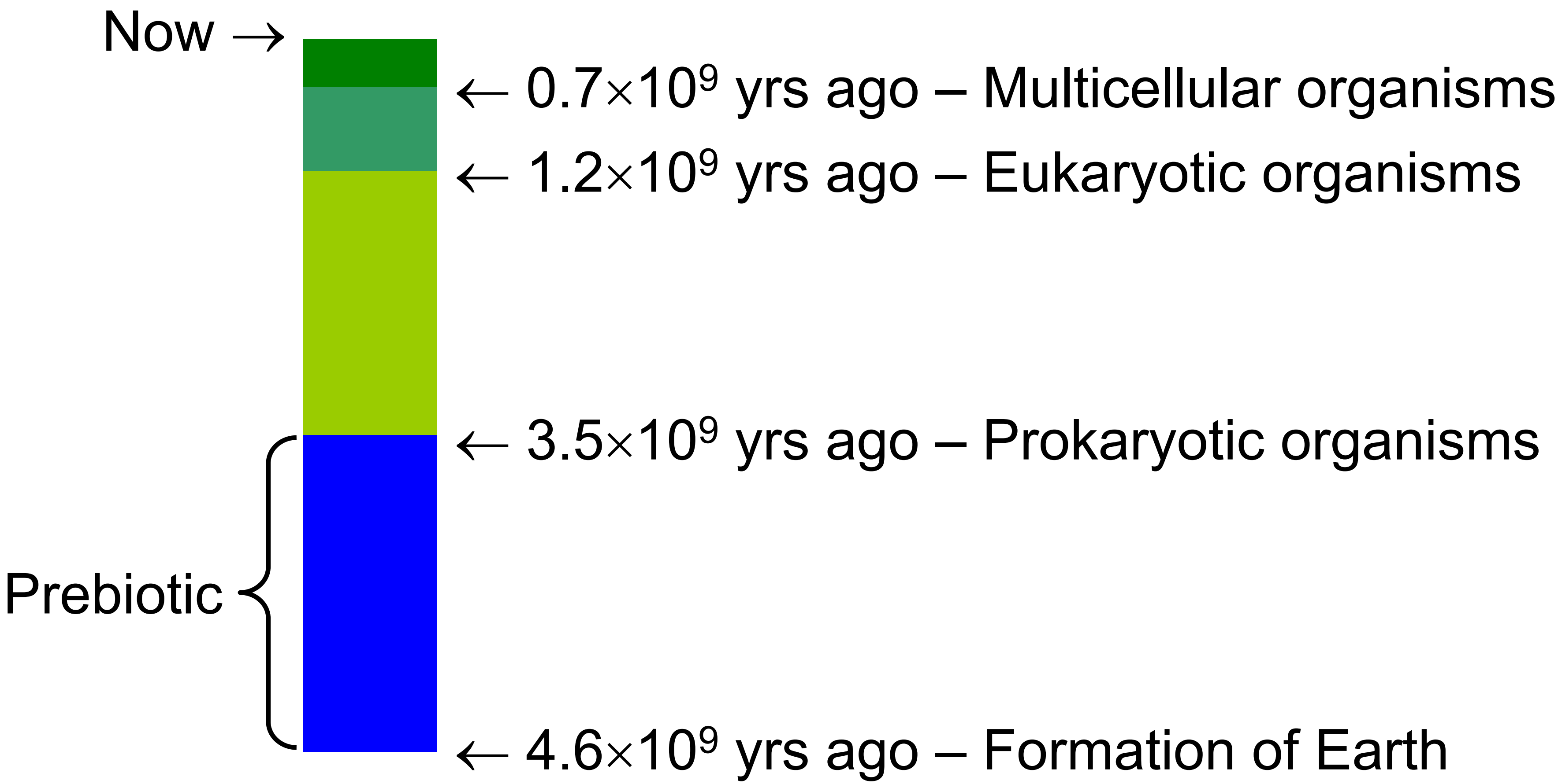
Sugar in the primordial soup

The formose reaction and the origin of life

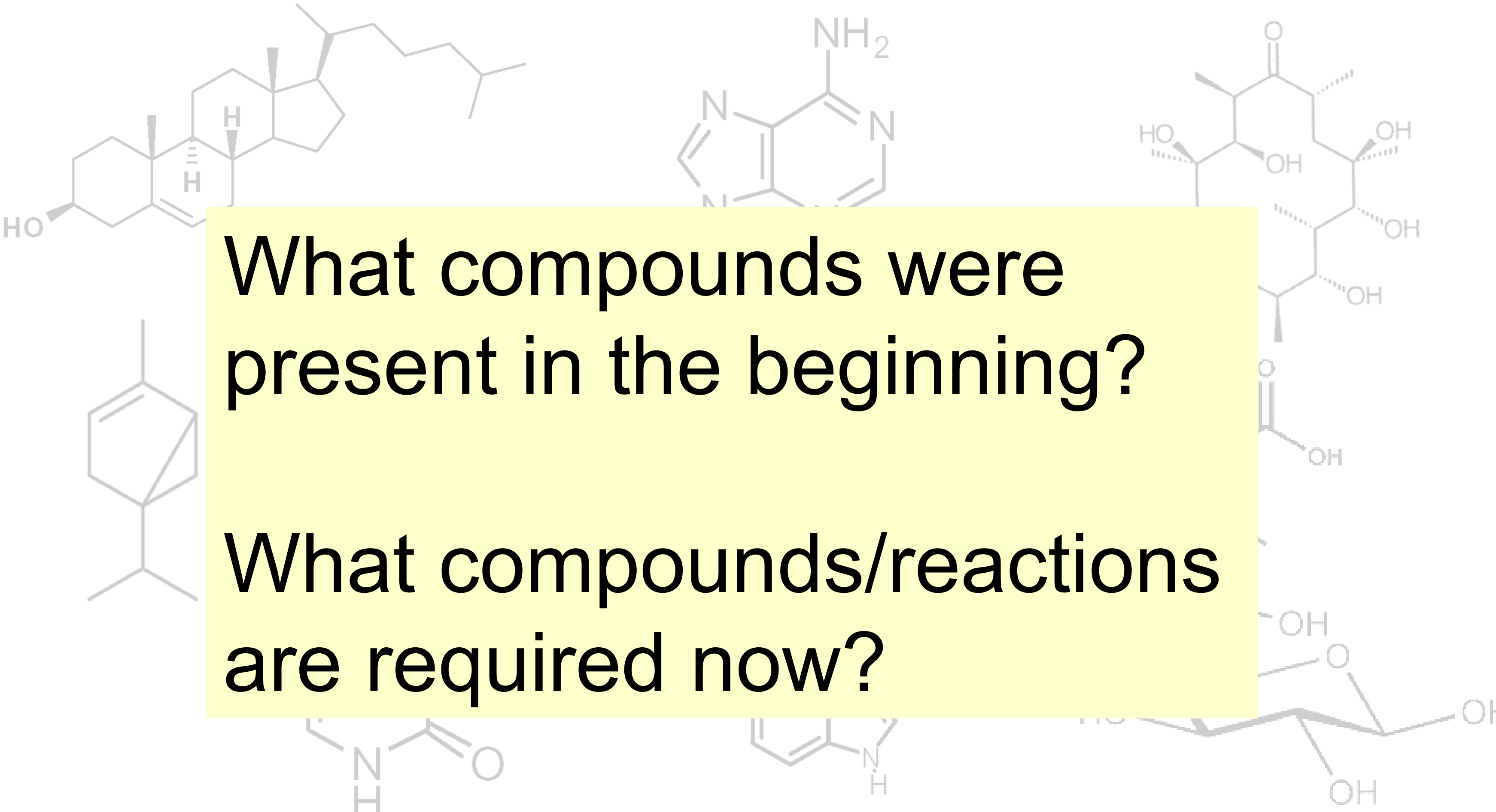
Content

- Life from the Soup
- Proteins *versus* RNA
- Prebiotic syntheses of amino acids & nucleobases
- Prebiotic synthesis of sugars
- Sugar in space
- Conclusion

Life on Earth



What started life?



What compounds were present in the beginning?

What compounds/reactions are required now?

The primordial "soup"

CH_2O CH_3CN N_2 CH_4

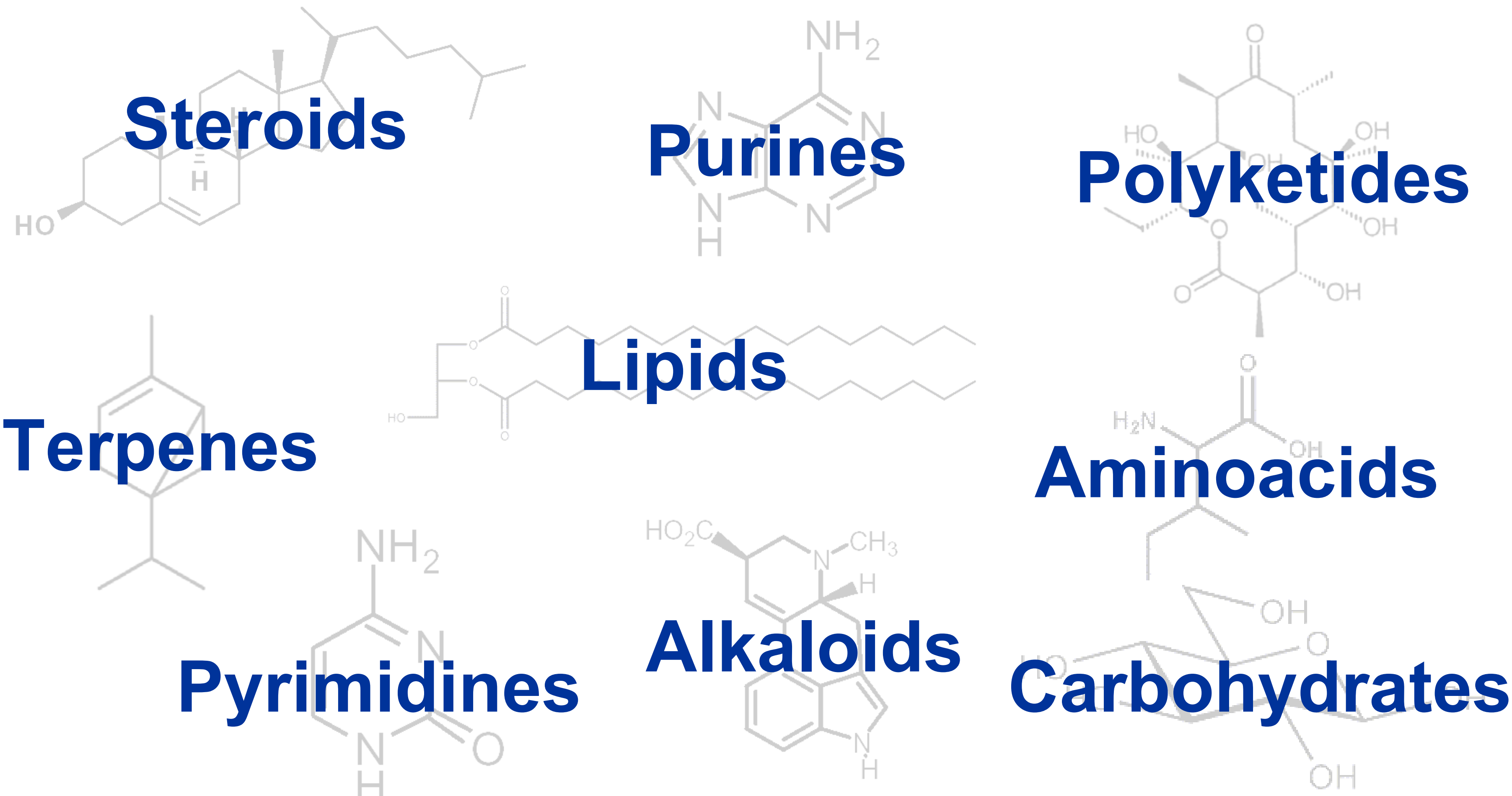
CO_2 CH_2CHCN $HCCCN$

$NCCN$ CO NH_3

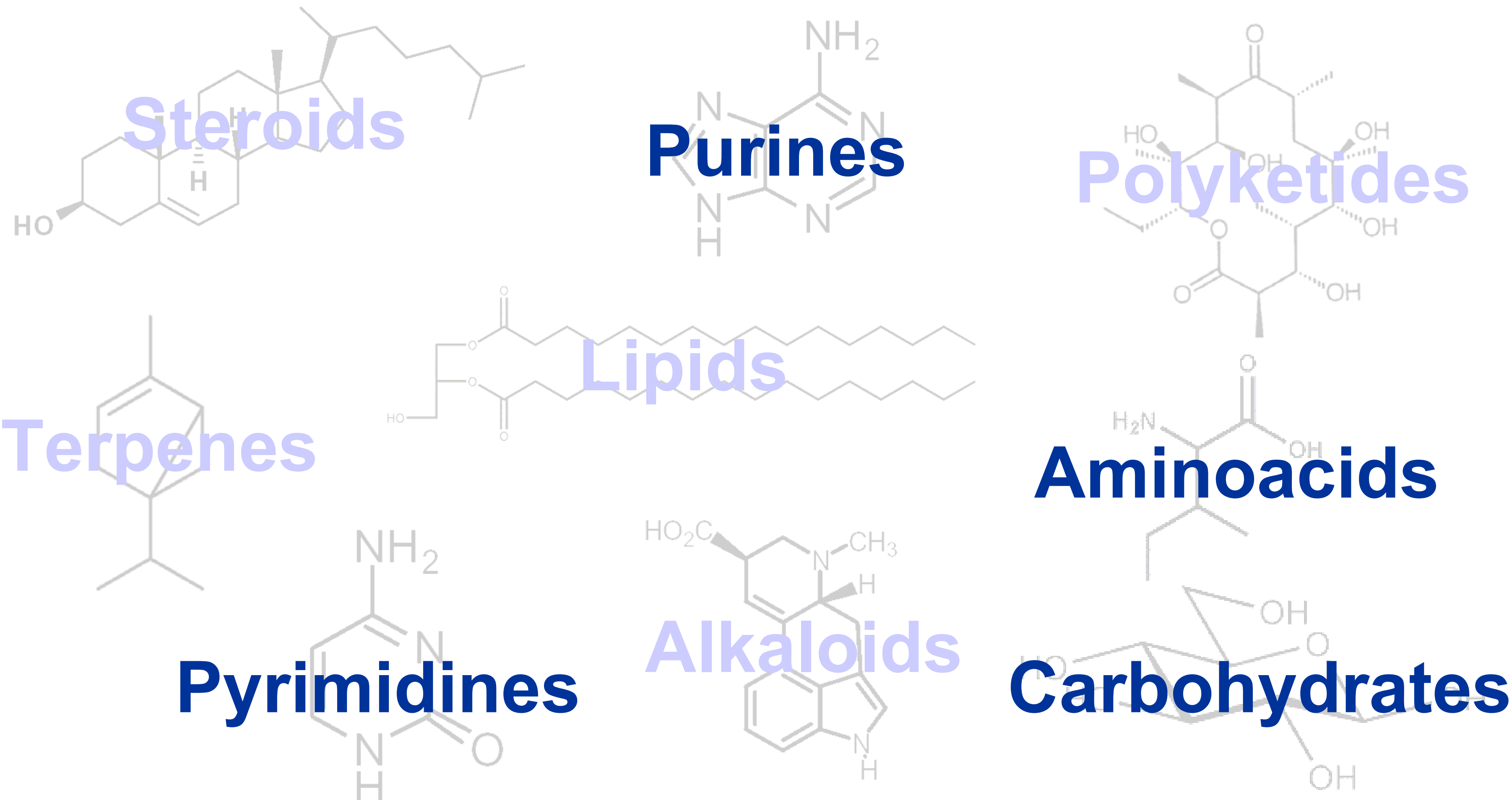
SO_2 H_2O HCN

Note: no photosynthesis - no O_2!

Natural products



Some are more important!



The essentials of (modern) life

Proteins

composed of amino acids

catalyse reactions

RNA

composed of nucleobases, ribose and phosphate

carry genetic information

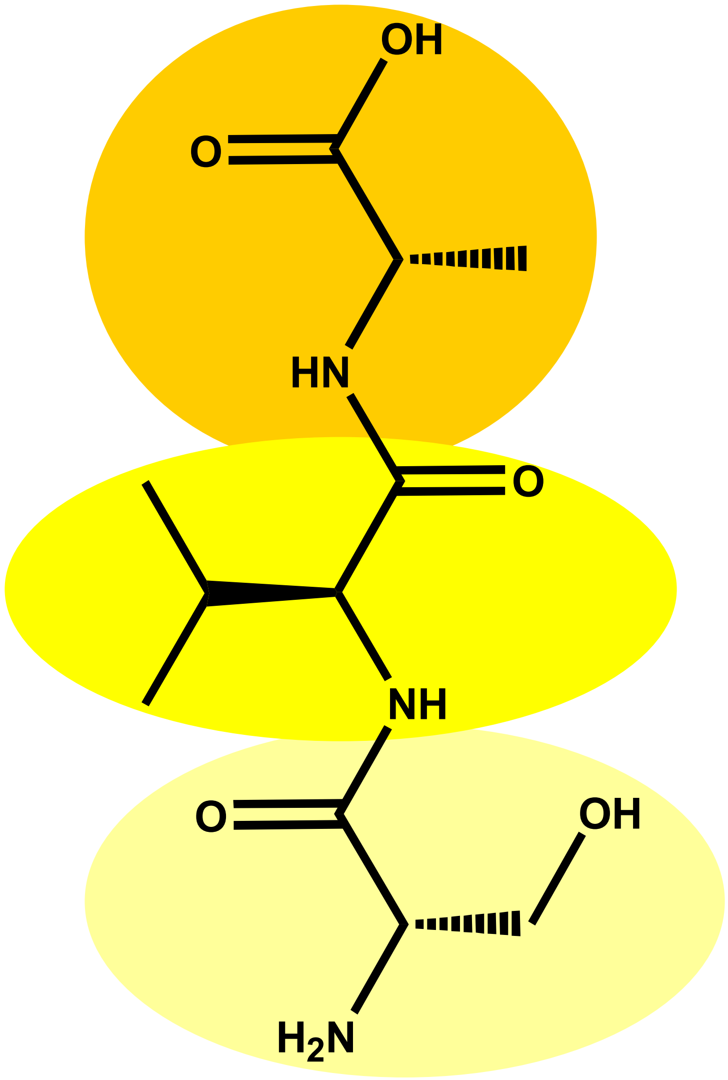
Which was first, RNA or proteins?

Proteins

– superior catalysts, simple building blocks, stable

RNA

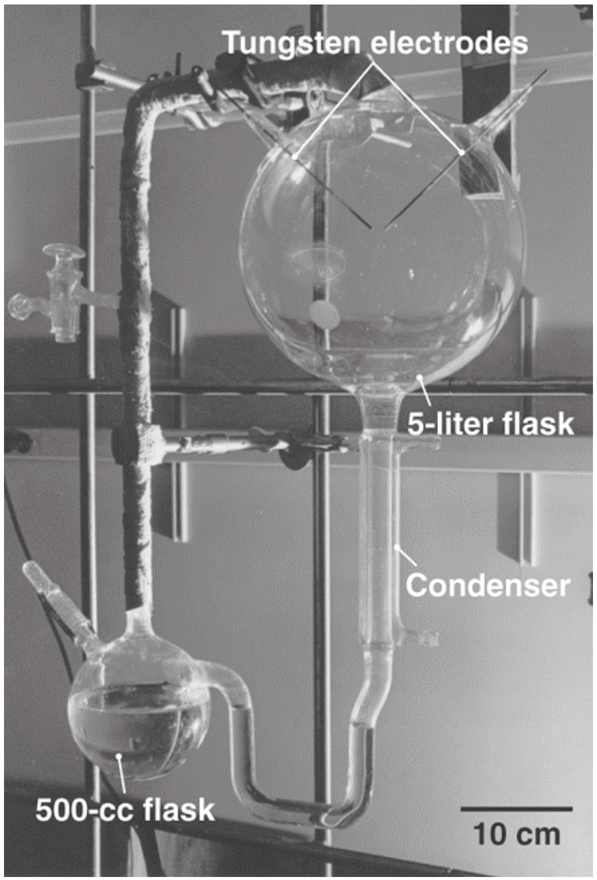
– can be catalysts, complex building blocks, unstable
but can replicate themselves

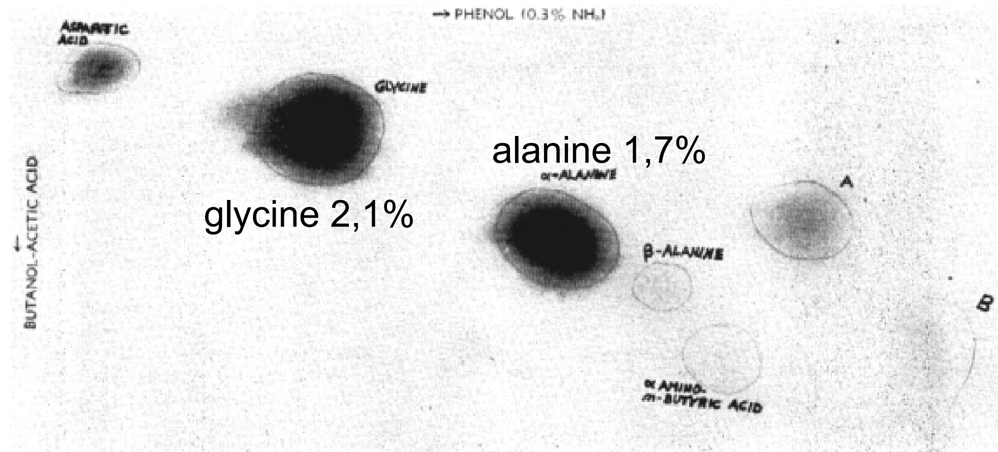


Protein

aminoacid

Prebiotic amino acid syntheses



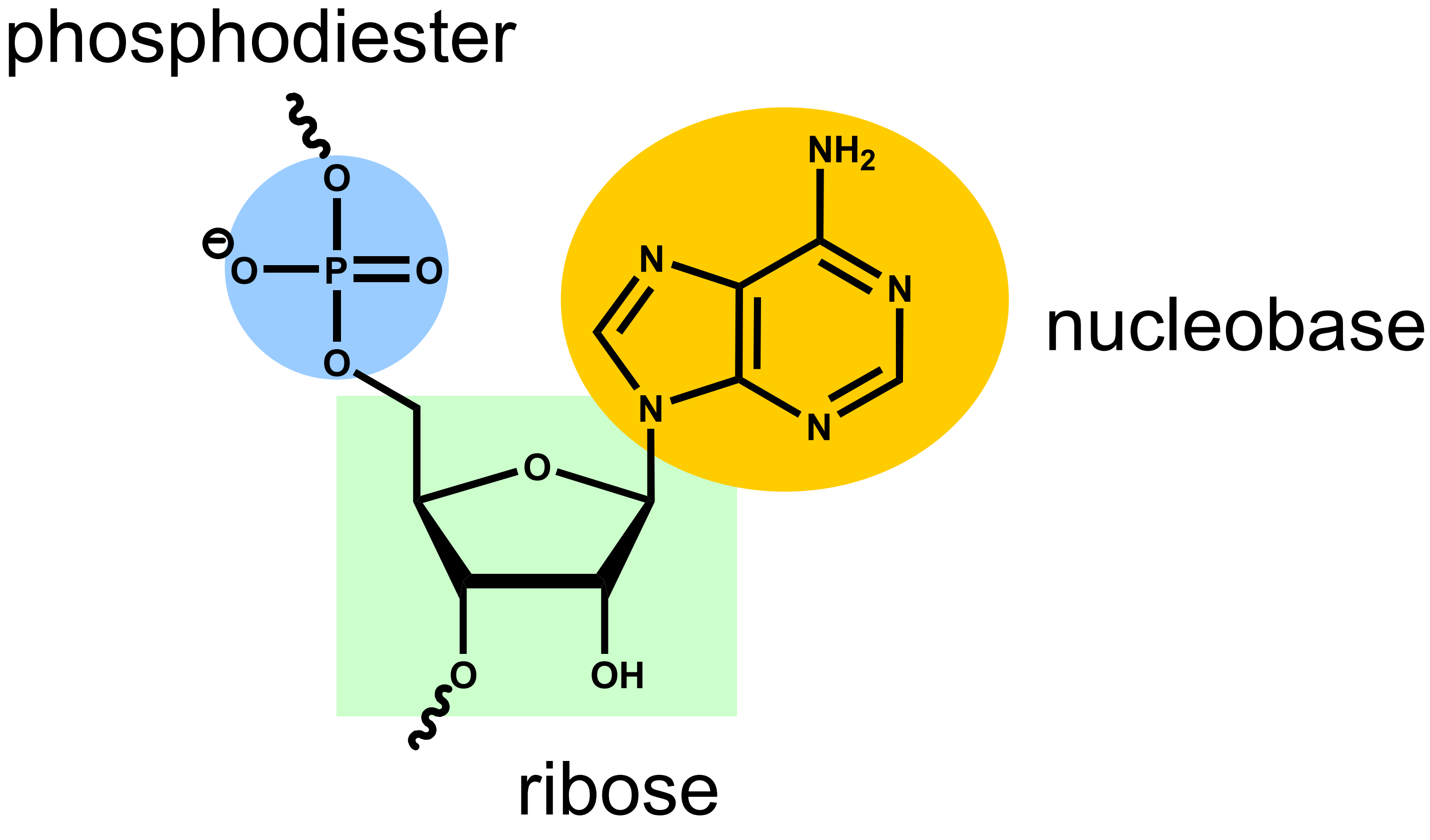


S.L. Miller

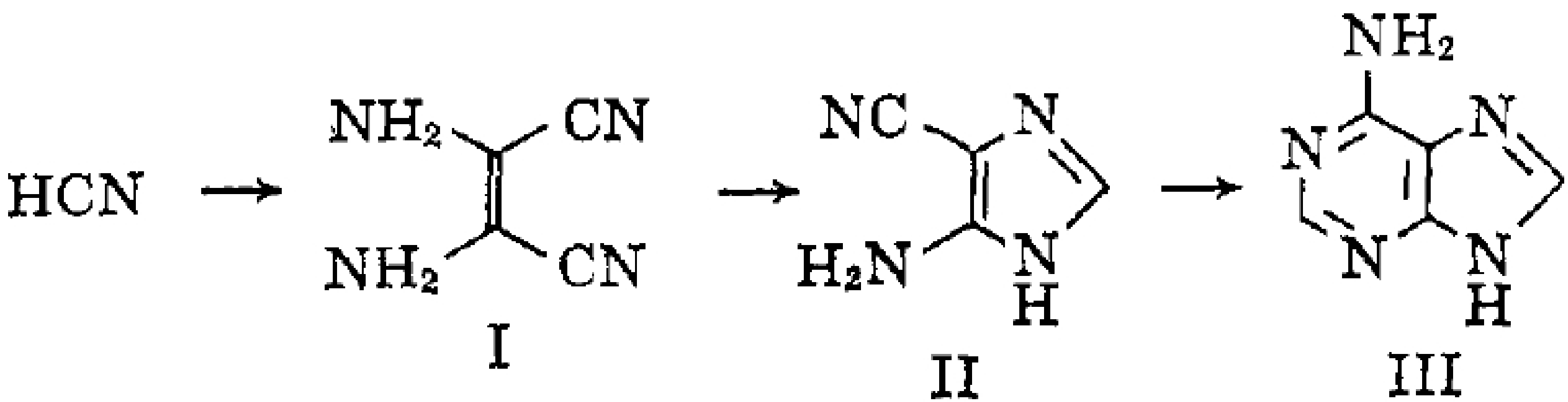
Science **117** (1952) 528-529

J. Am. Chem. Soc. **77** (1955) 2351-2361

RNA



Prebiotic nucleobase syntheses

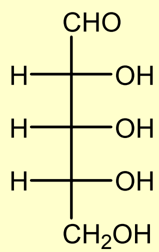


J. Oró, *Nature* **191** (1961) 1193-1194

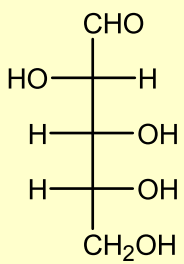
Common monosaccharides

aldopentoses

ribose

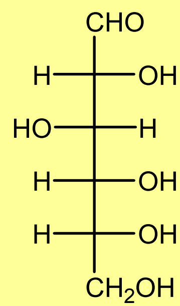


arabinose

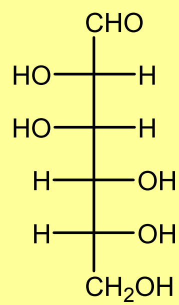


aldohexoses

glucose

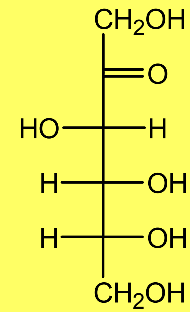


mannose



ketohexose

fructose



Prebiotic carbohydrate synthesis:

The Formose reaction

$$CH_2O \xrightarrow{^{\ominus}OH} (CH_2O)_n$$

A. Butlerow, *Liebigs Ann. Chem.* **53** (1861) 295-298
O. Leow, *J. prakt. Chem.* **33** (1886) 321-351

Some of the reactions involved

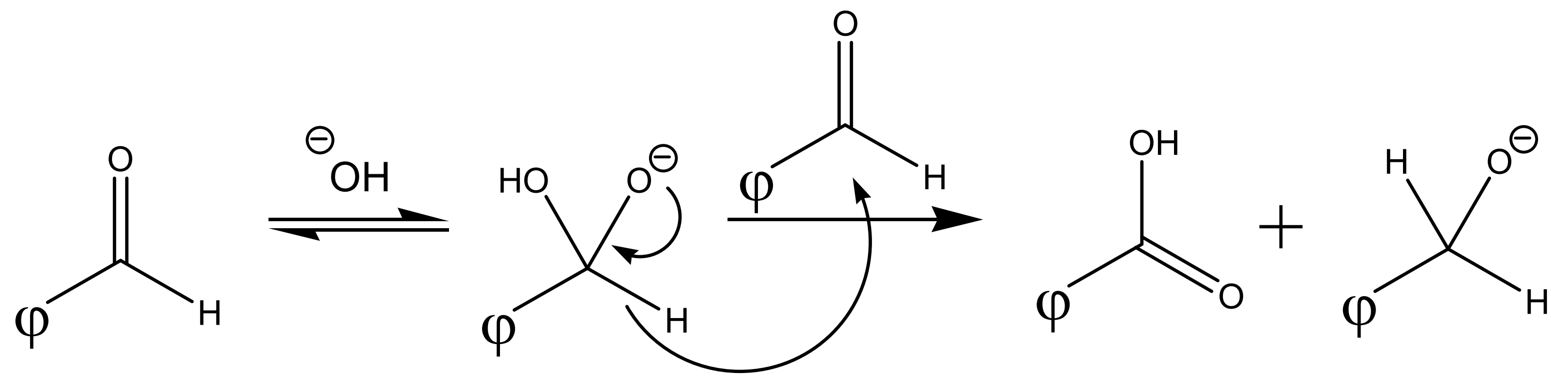
Cannizzaro

de Bruyn-van Ekenstein

Aldol condensation

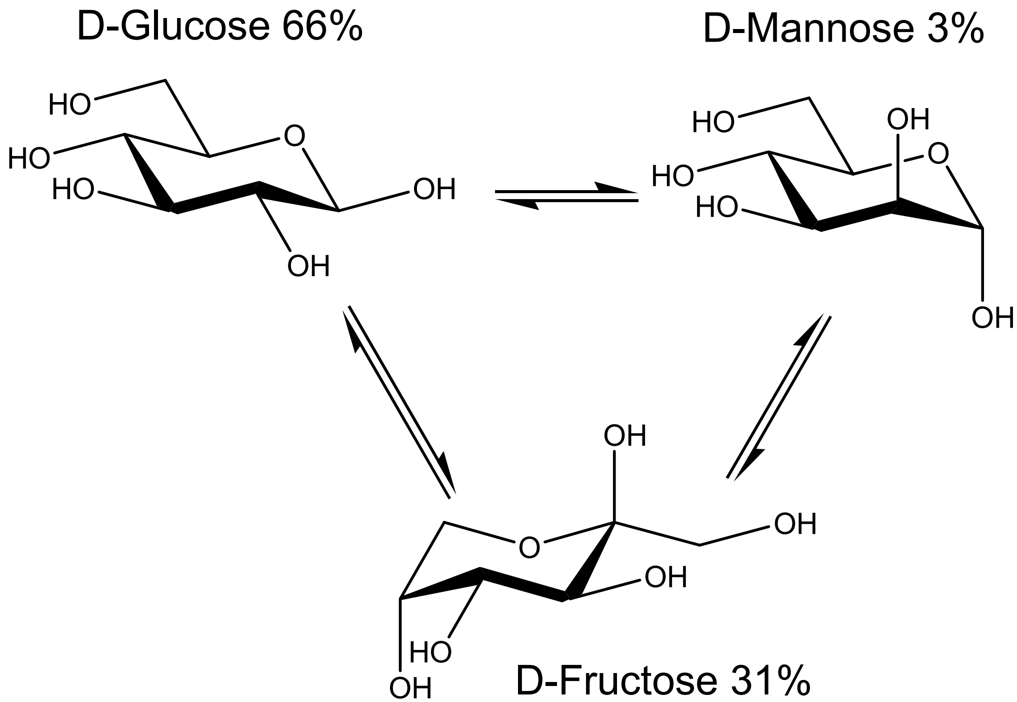
Retro-aldol

Cannizzaro reaction



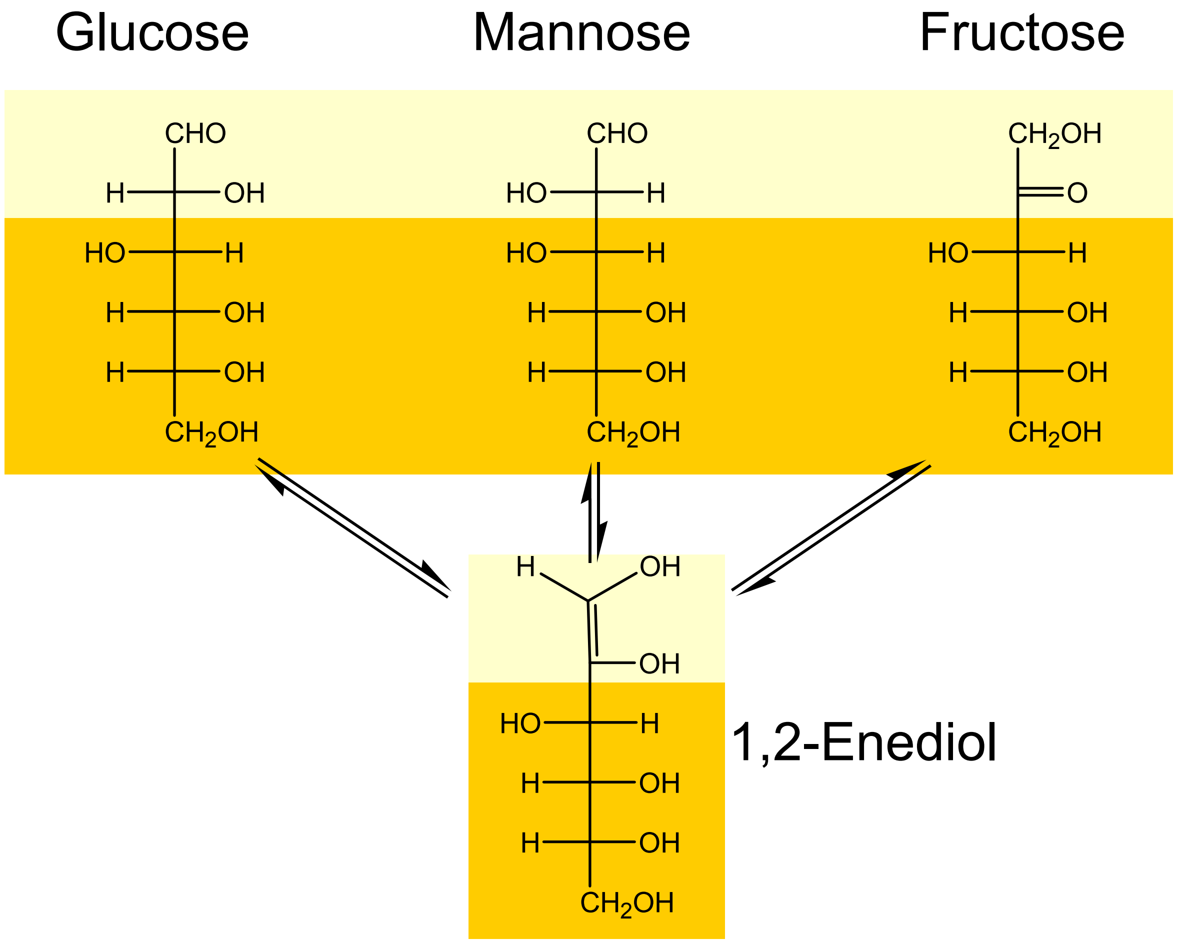
Cannizzaro, *Ann.* **88** (1853) 129-

de Bruyn-van Ekenstein rearrangement

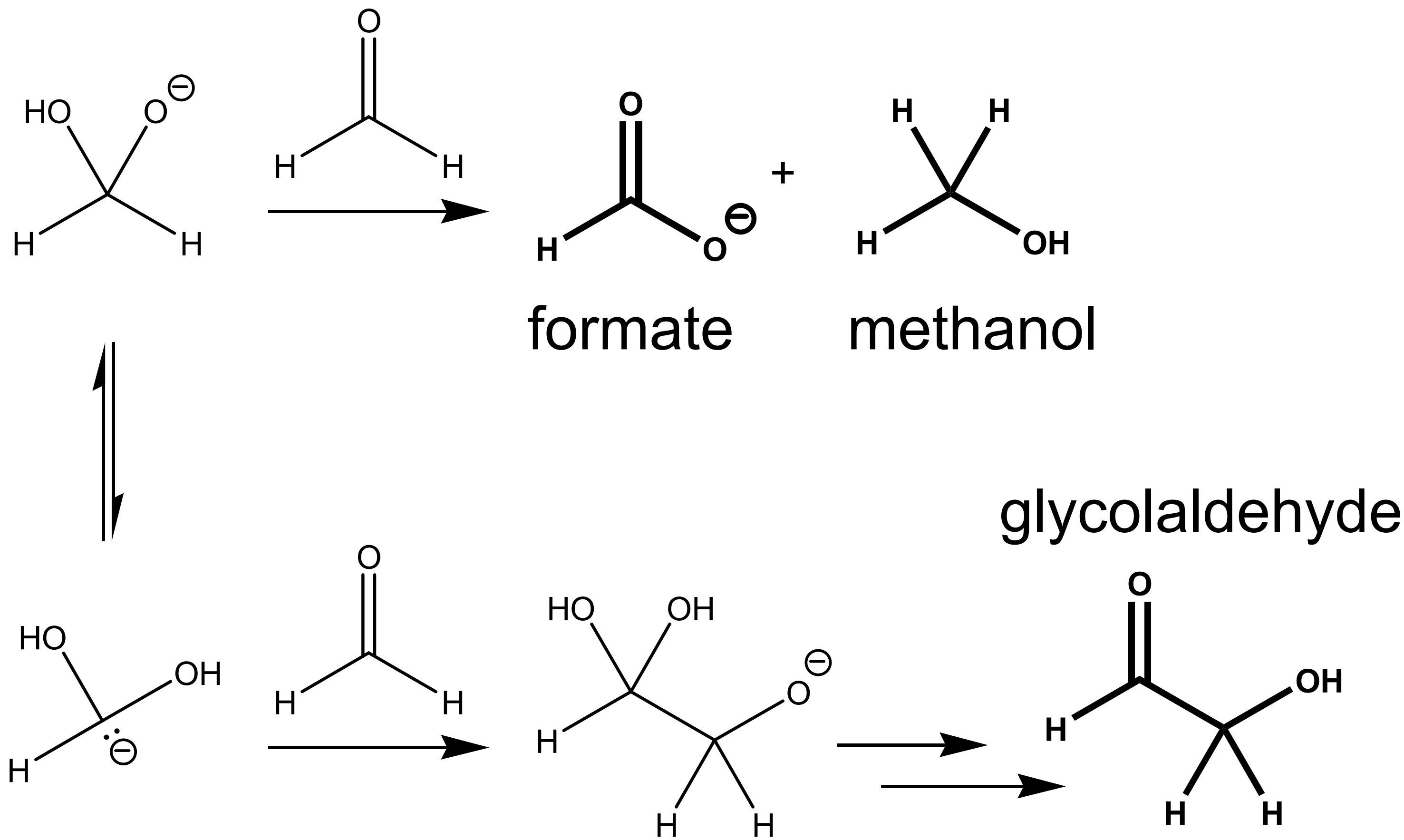


de Bruyn, *Rec. Trav. Chim.* 14 (1895) 150-
Evans, *Chem. Rev.* **31** (1942) 537-559

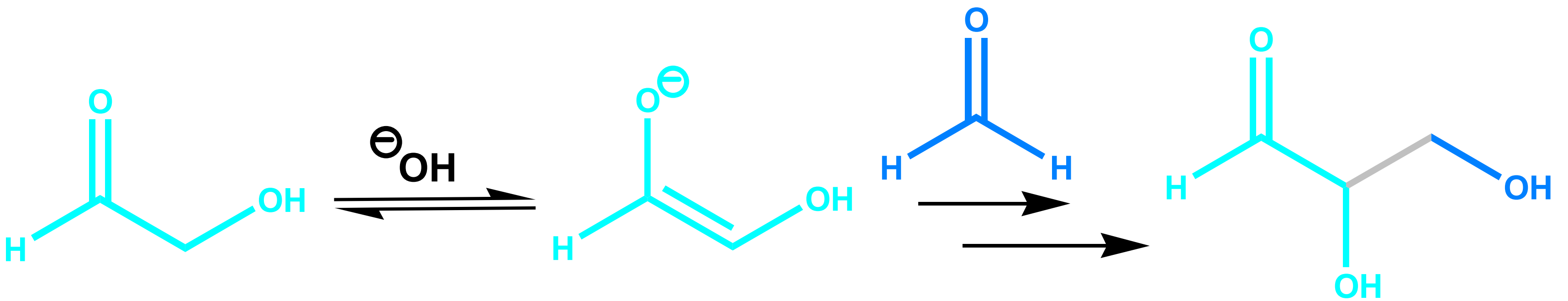
de Bruyn-van Ekenstein mechanism



The first step...

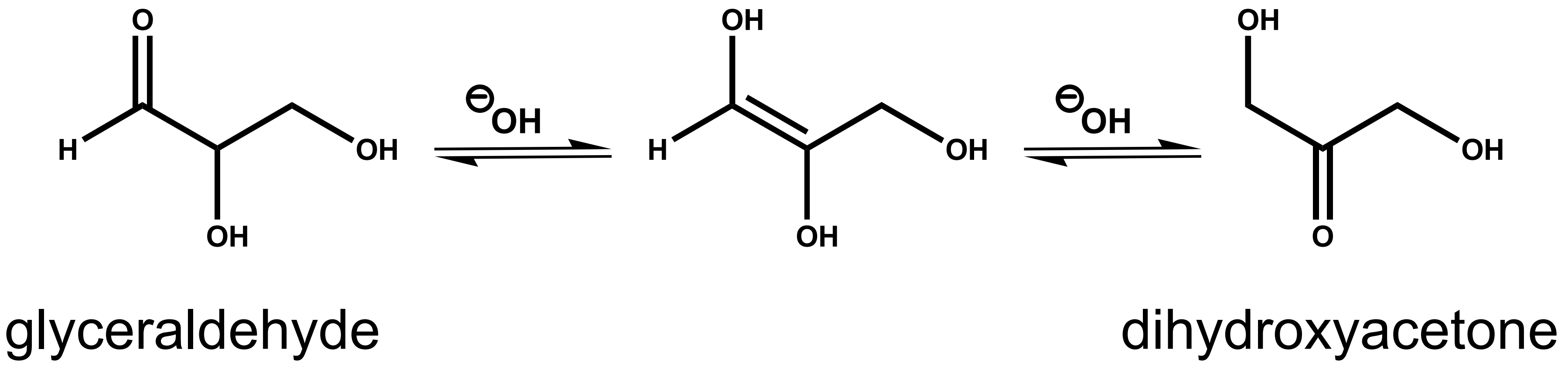


Aldol condensation

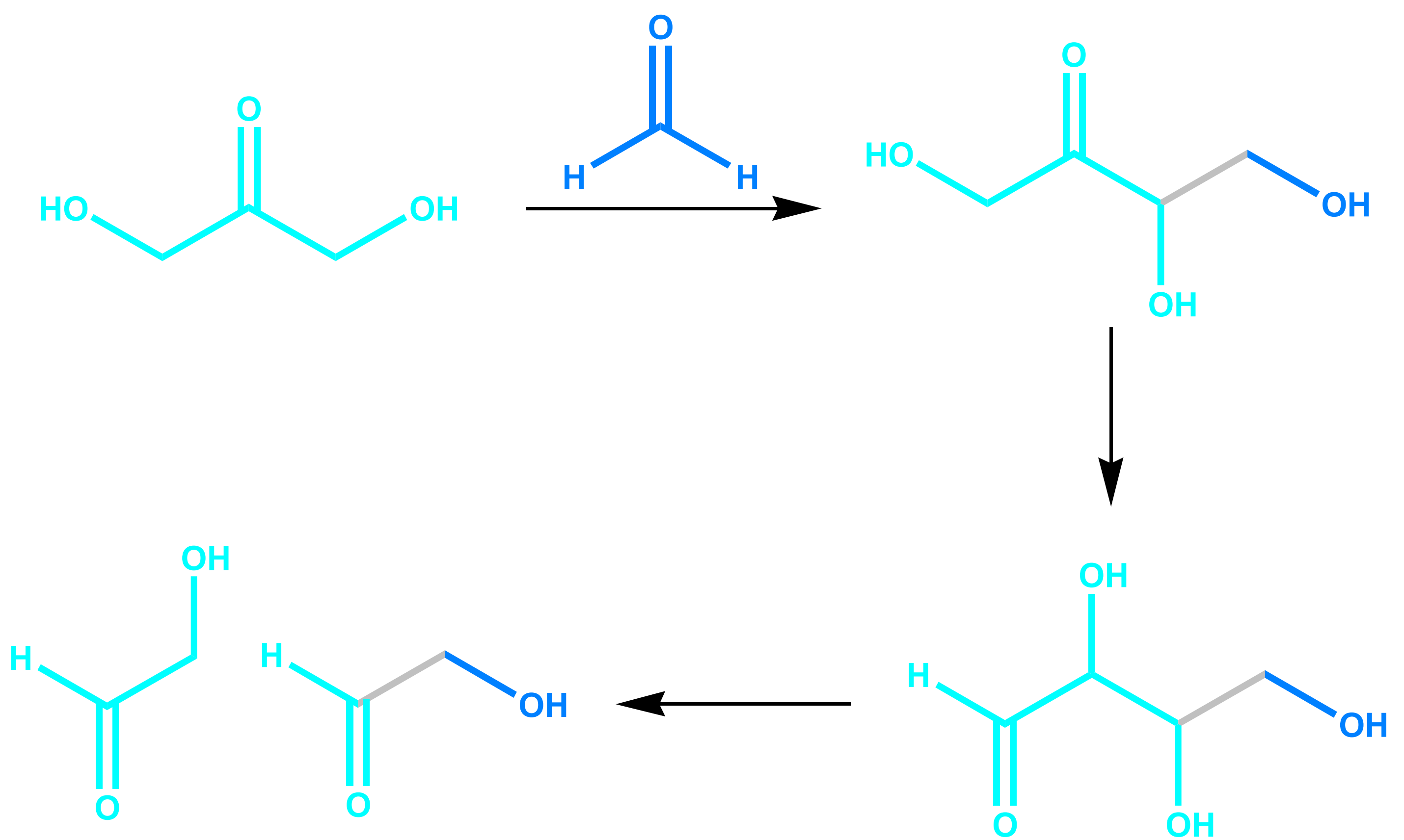


glyceraldehyde

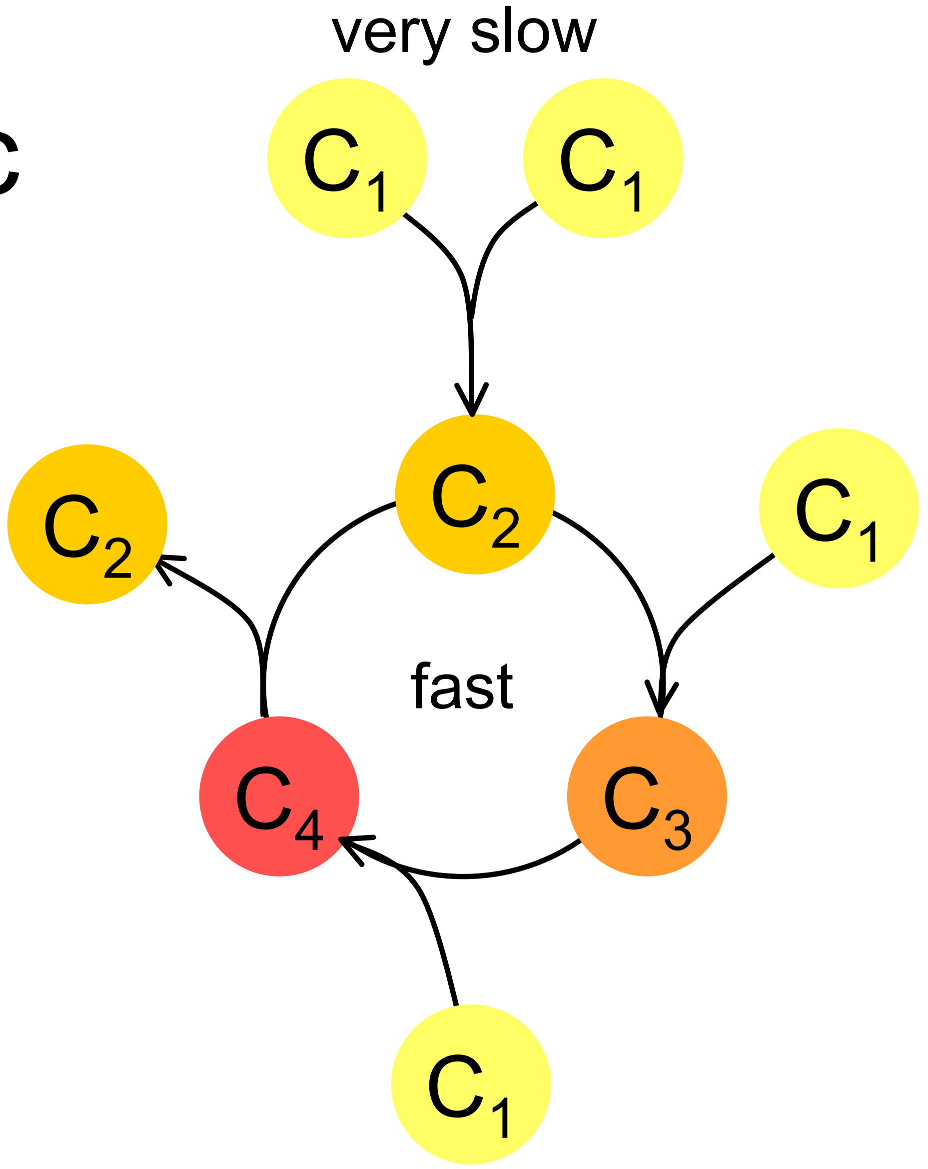
de Bruyn-van Ekenstein



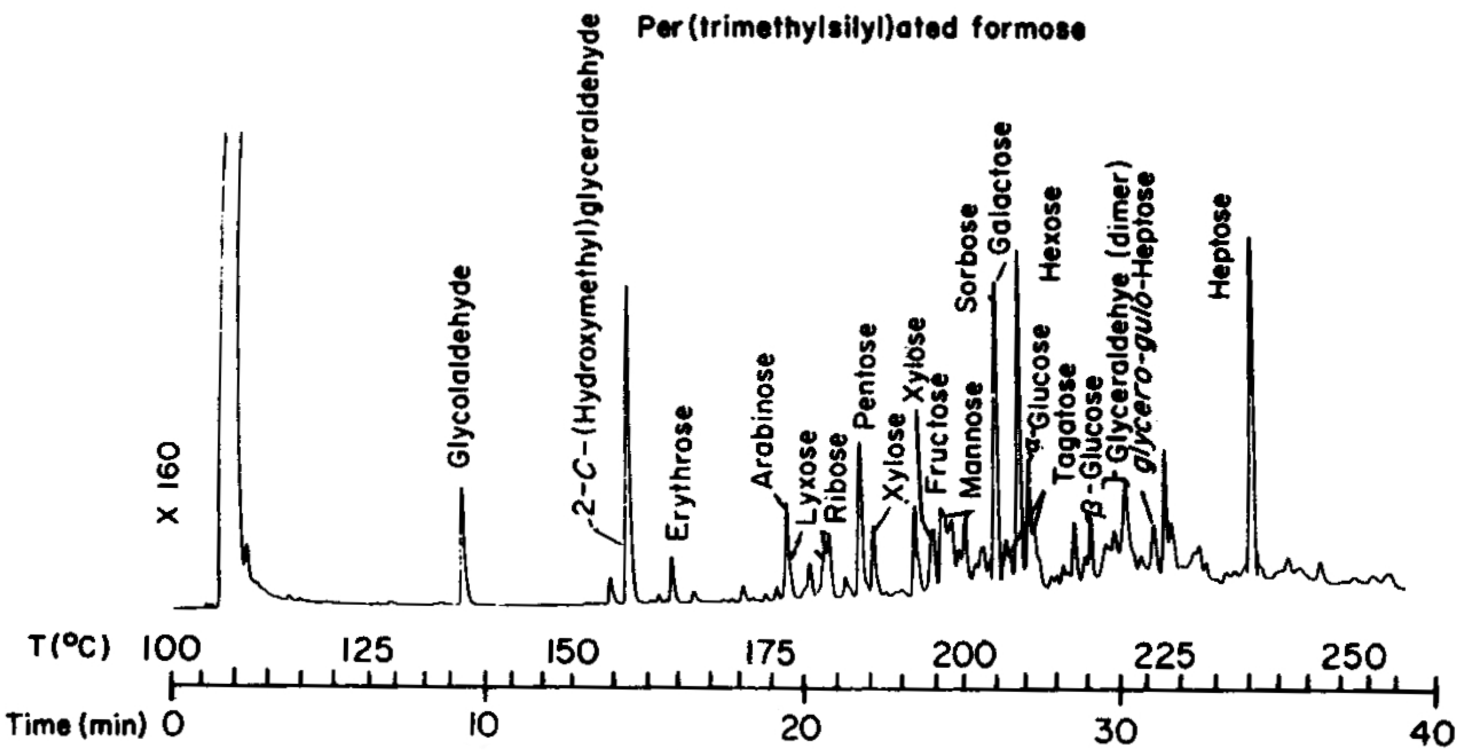
$$C_3 + C_1 \rightarrow C_2 + C_2$$



Autocatalytic cycle



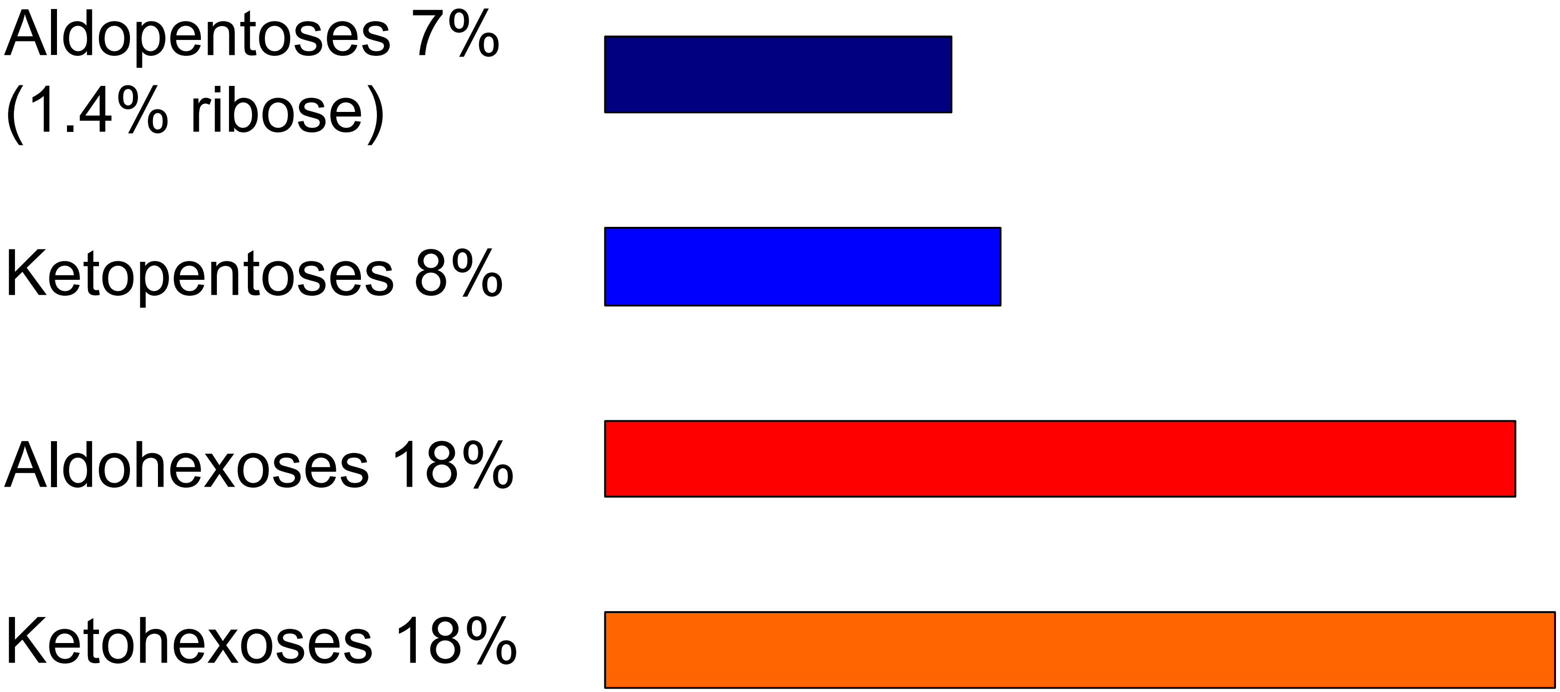
The result:



Per(trimethylsilyl)ated formose
X 160
Glycolaldehyde
2-C-(Hydroxymethyl)glyceraldehyde
Erythrose
Arabinose
Lyxose
Ribose
Pentose
Xylose
Xylose
Fructose
Mannose
Sorbose
Galactose
α-Glucose
Hexose
Tagatose
β-Glucose
Glyceraldehye (dimer)
glycero-gulo-Heptose
Heptose
T(°C) 100 125 150 175 200 225 250
Time (min) 0 10 20 30 40

Sugars in formose

(55% total yield of sugars)

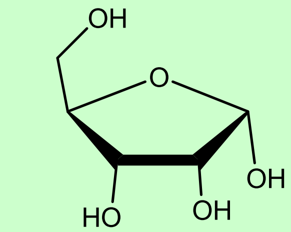


Open chain forms

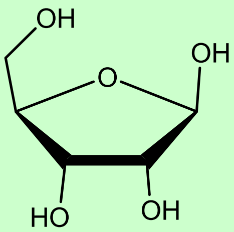
	aldoses	ketoses
tetroses	11-16%	100%
pentoses	0.1-0.2%	8-22%
hexoses	0.002-0.1%	0.3-0.7%

Tautomers of D-ribose

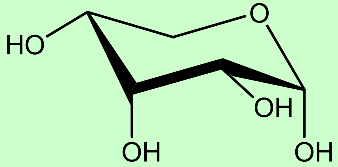
Cyclic forms (99,9%)



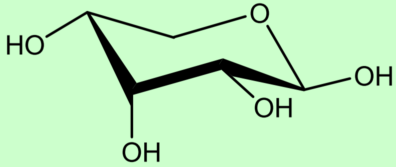
α-furanose



β-furanose

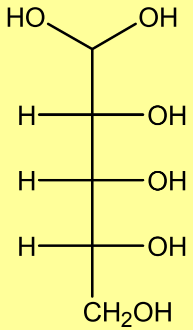


α-pyranose

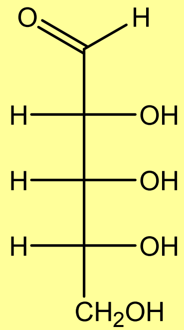


β-pyranose

Acyclic forms (0,1%)



hydrate



aldehyde

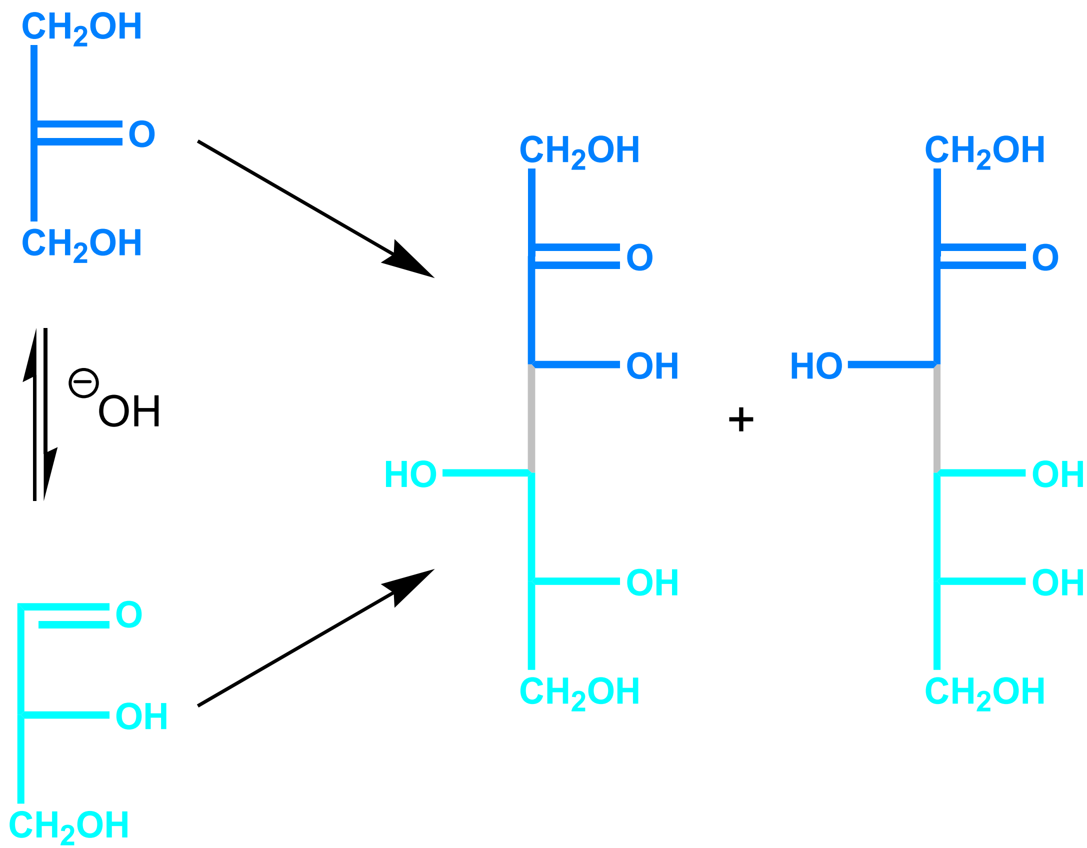
Problems

Much more hexoses than pentoses

Very little ribose

Racemic mixture of sugars

dihydroxyacetone



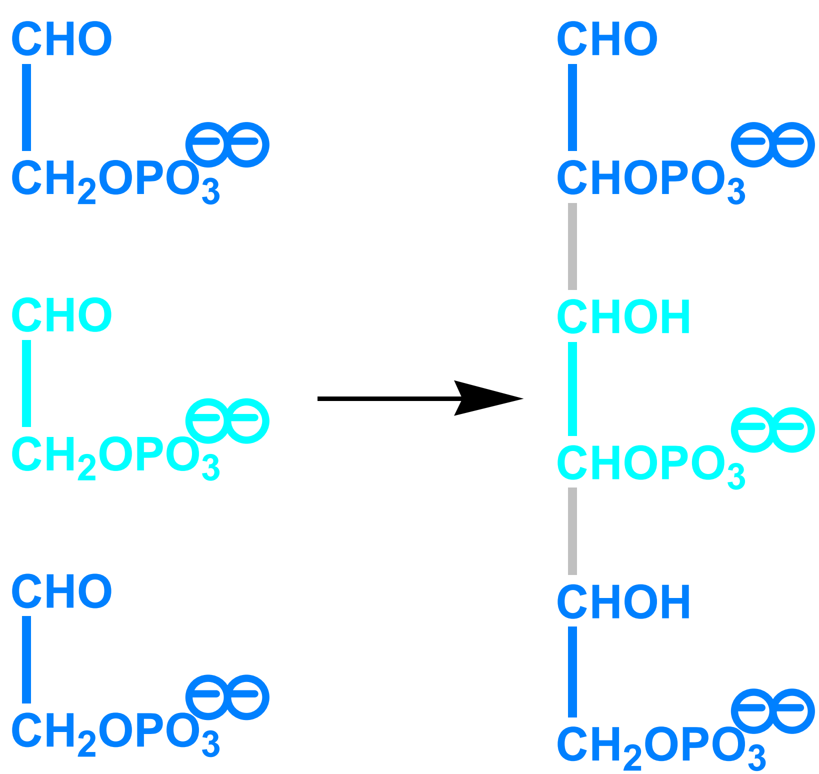
D-glyceraldehyde

D-sorbose
26%

D-fructose
34%

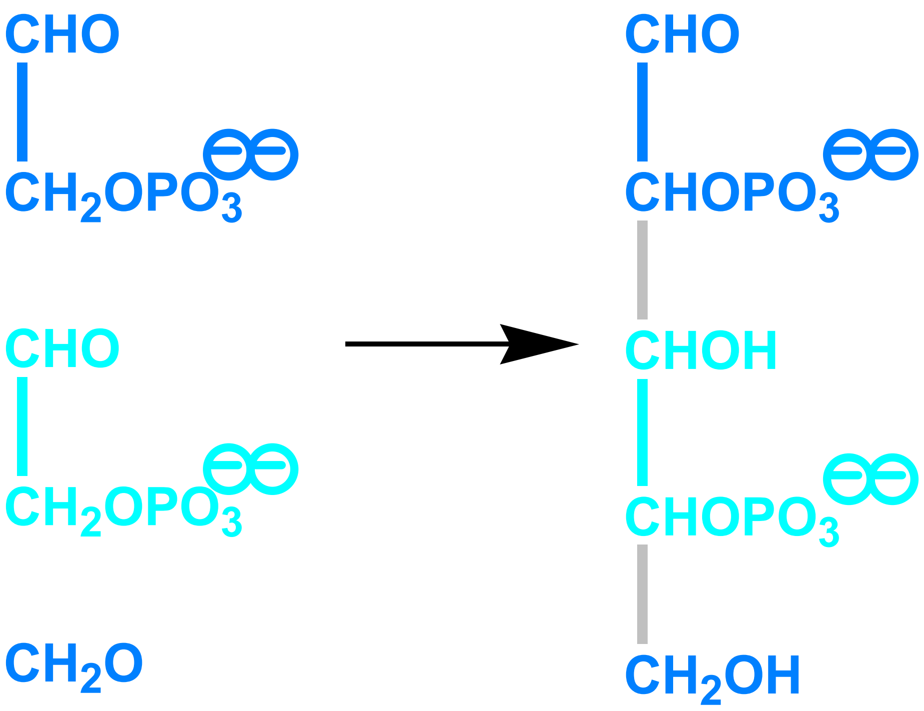
H.O.L. Fischer & E. Baer, *Helv. Chim. Acta* **19** (1936) 519-532

Glycolaldehyde phosphate 1



Müller et al., *Helv. Chim. Acta* **73** (1990) 1410

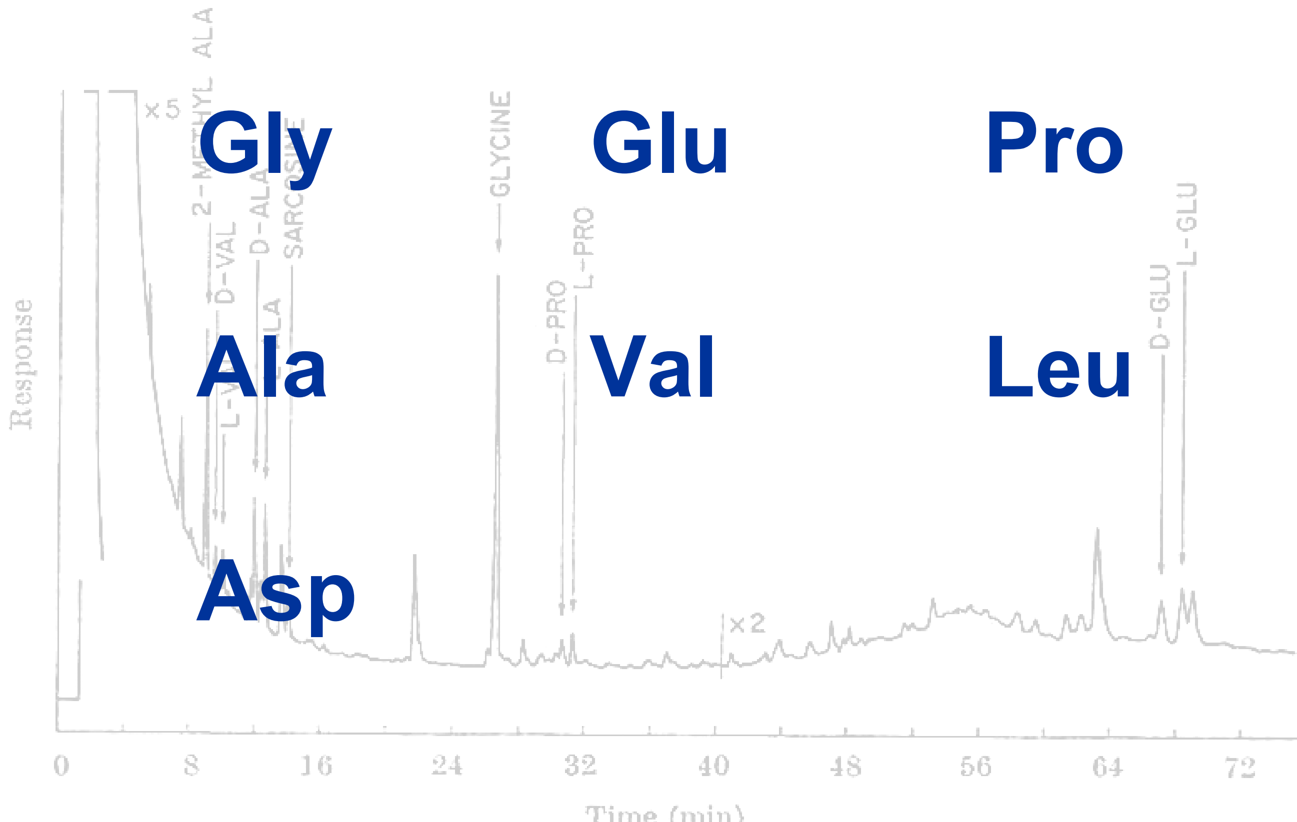
Glycolaldehyde phosphate 2



Extraterrestial compounds

Aminoacids	60 ppm
Carbohydrates	60
Pyrimidines	0.06
Purines	1.2

Aminoacids



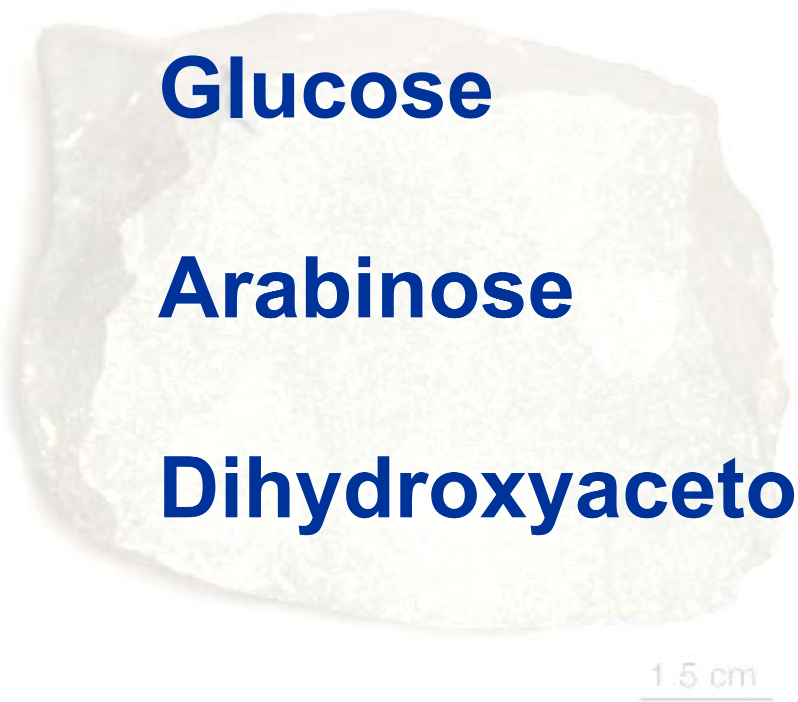
Gly **Glu** **Pro**

Ala **Val** **Leu**

Asp

+12 not found in proteins

Carbohydrates



Glucose

Mannose

Arabinose

Xylose

Dihydroxyacetone

+ aldonic acids & alditols

Conclusion

The basic building blocks of proteins and RNA can be prepared from compounds expected to be present on early Earth.

The conditions to make them are incompatible, *i.e.* they can not be formed under the same reaction conditions and in the same place.

The strongest proof that they could have been formed prebiotically is their presence in extraterrestrial matter.