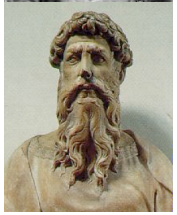
# Background

Platonic Hydrocarbons
Ryan Shenvi

The knowledge at which geometry aims is knowledge of the eternal, and not of aught perishing and transient . . . My noble friend, geometry will draw the soul towards truth, and create the spirit of philosophy, and raise up that which is now unhappily allowed to fall down. . . Nothing should be more sternly laid down than that the inhabitants of your fair city by all means learn geometry.

–Plato (*ca.* 427-347 BC)
"The Republic," ca. 370 BC



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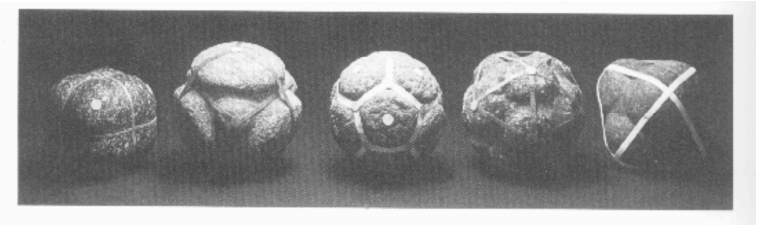
–St. John, (ca. 10 AD-100 AD)
"The Gospel of John," ca. 96 AD

## *What are the 'platonic hydrocarbons'?*

Platonic Solids:
- Regular solids, regular polyhedra: convex polyhedra whose faces are equivalent, convex regular polygons.
- Discovered 'first' by the neolithic Scots, *ca.* 1300-1400 BC.



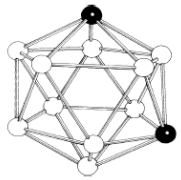
- Described mathematically by Theaetetus (417 BC-369 BC), who *proved* the existance of 5 *and only* 5 regular solids; included in Euclid's Elements, *Book X.*

| Polyhedron | Faces | Edges | Vertices | Symmetry Group |
|---|---|---|---|---|
| Tetrahedron | 4 | 6 | 4 | $T_d$ |
| Hexahedron | 6 | 12 | 8 | $O_h$ ↻ geometric duals |
| Octahedron | 8 | 12 | 6 | $O_h$ ↻ |
| Dodecahedron | 12 | 30 | 20 | $I_h$ ↻ geometric duals |
| Icosahedron | 20 | 30 | 12 | $I_h$ ↻ |

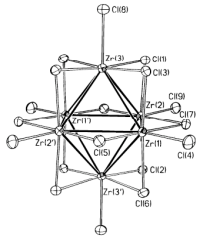
- Included in Plato's Timaeus as part of his 'theory of everything,' which assigned the regular geometry of the solids to each of the elements: earth, water, air, fire, and ether (an element of order or logic added to the original elements described by Emedocles of Agrigentum, 495-435 BC).
- In 1852, Schläfli proved the existance of exactly six regular polyhedra in four dimensions and three in all higher dimensions (some may be familiar with the hypercube, or tesseract, of A Wrinkle in Time fame).

*Platonic hydrocarbons* are the corresponding carbogens, where each vertex is a carbon, each edge a bond, and each face a ring.

- Not all platonic solids translate to platonic hydrocarbons; limited by carbon valence, bonding angles, and strain. Octahedrane and icosahedrane have not been prepared, nor has unsubstituted tetrahedrane.
- However, numerous inorganic molecules adopt these geometries:

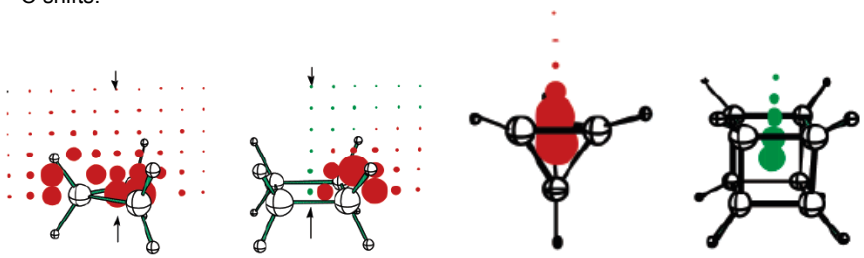


$C_2B_{10}H_{12}$
carboranes



$[Zr_6Cl_{18}]^{3-}$

- Tetrahedrane and cubane have been called "super □-aromatic and super □-antiaromatic, respectively:
  Cyclopropane exhibits strong □-aromaticity as evidenced by its **1.** large diamgnetic susceptibility and anisotropy, **2.** upfield shifts of attached protons, **3.** shielding of protons above its ring and **4.** a stabilization of 11.3 kcal/mol (compare 33.2 kcal/mol for benzene). Cyclobutane exhibits strong □-antiaromaticity: **1.** similarity to cyclopropane's strain (27.5 vs. 26.5 kcal/mol), **2.** abnormally low diamagnetic susceptibility, **3.** deshielded $^1H$ and $^{13}C$ shifts.



Planar cyclopropane, cyclobutane, tetrahedrane, and cubane dissected nucleus-independent chemical shift grids. Red and green points denote positive and negative NICS values, respectively

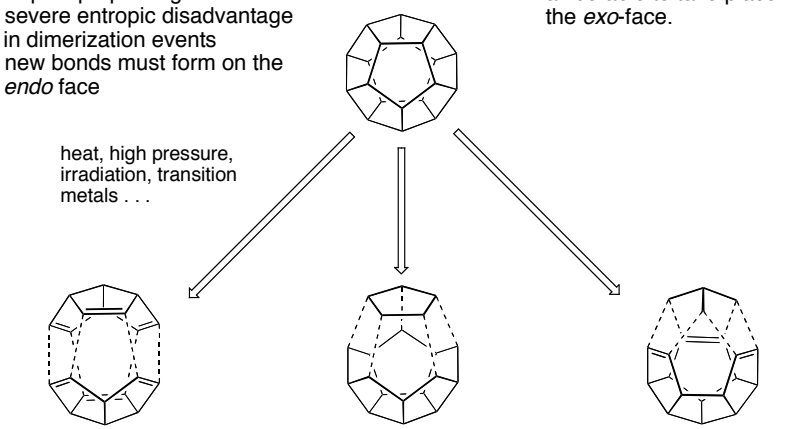
# Dodecahedrane



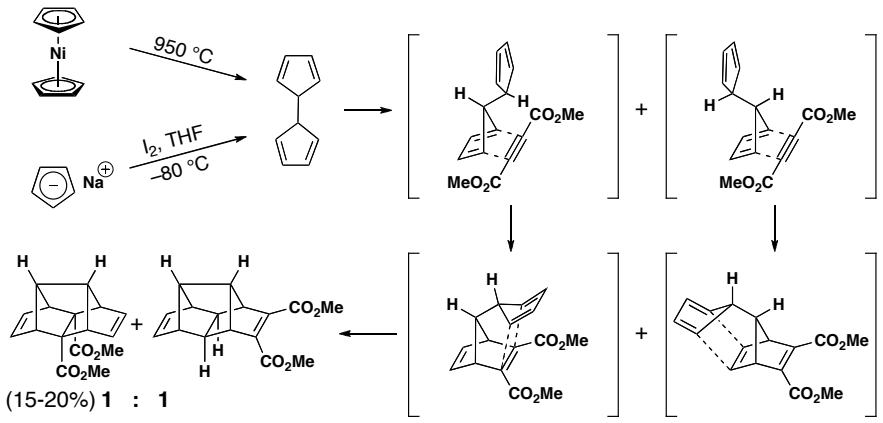
## *DODECAHEDRANE*

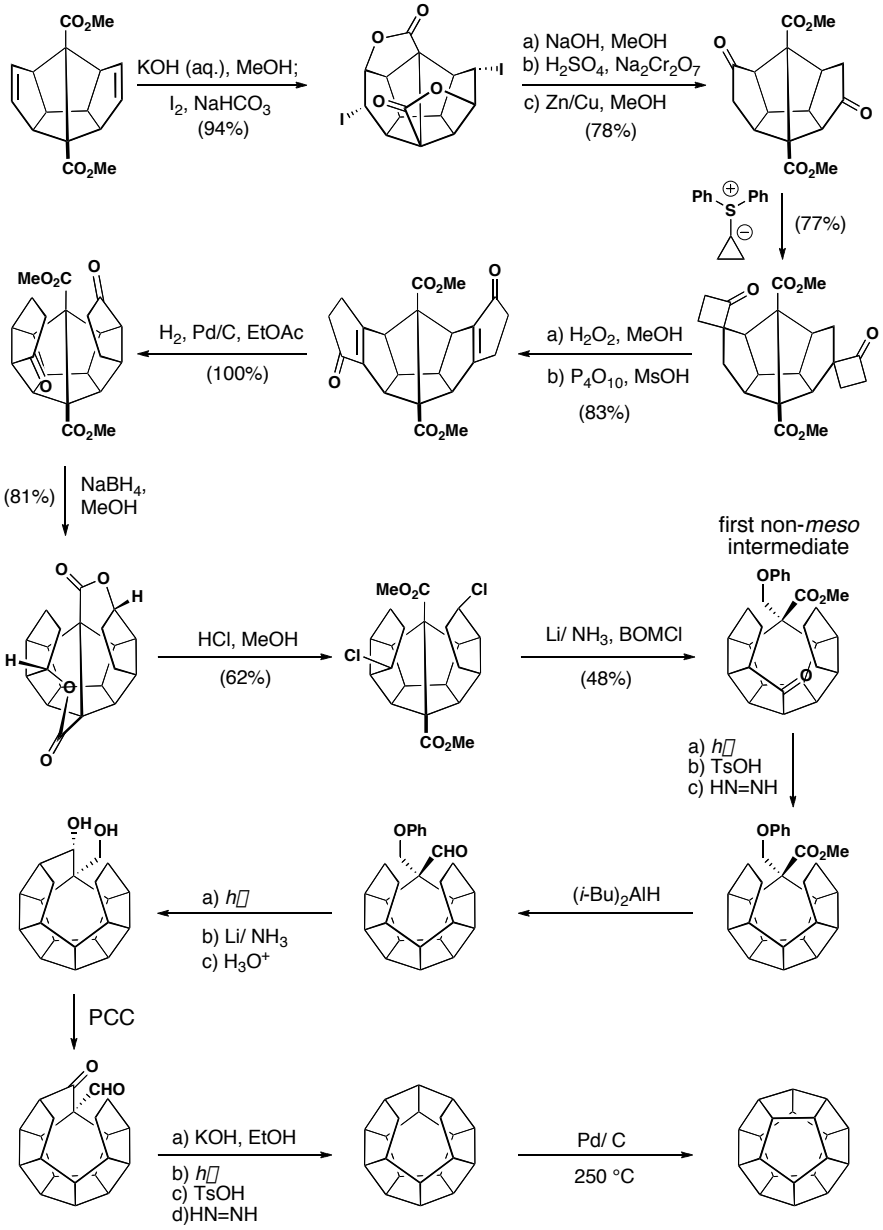
Considerations:
- tandem bond-forming events require proper alignment
- severe entropic disadvantage in dimerization events
- new bonds must form on the *endo* face

Late-stage reactions must all be able to take place from the *exo*-face.




SUCCESS!
Paquette, L. A.; Ternansky, R. J.; Balogh, D. W. *JACS*, **1982**, *104*, 4502

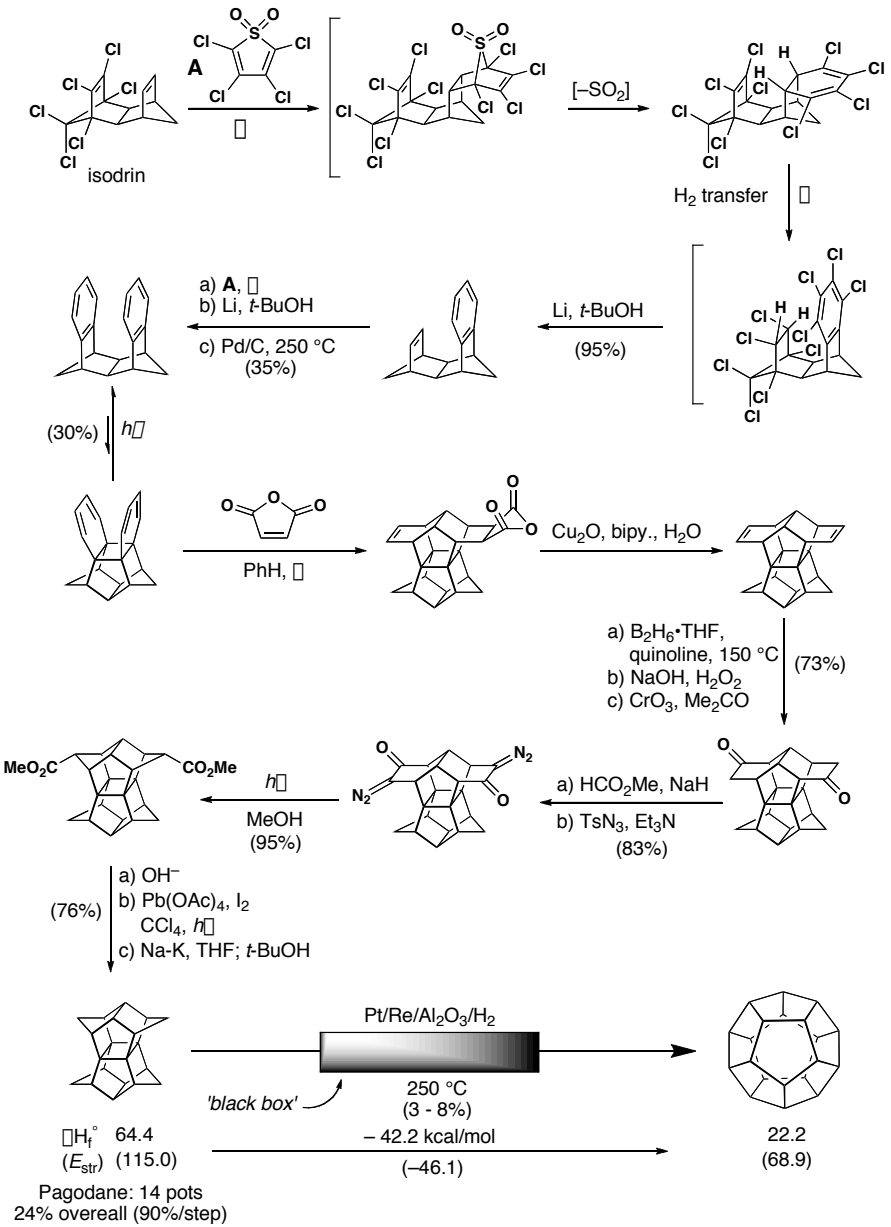


# Dodecahedrane

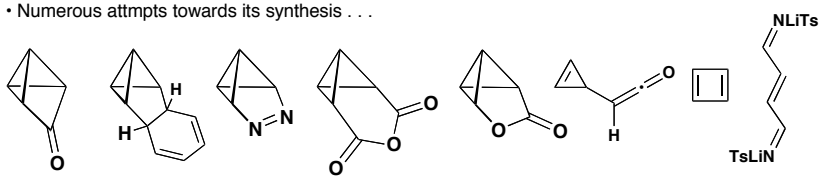


Prinzbach *et al. Angew. Chem. Int. Ed. Engl.* **1994**, 2239.



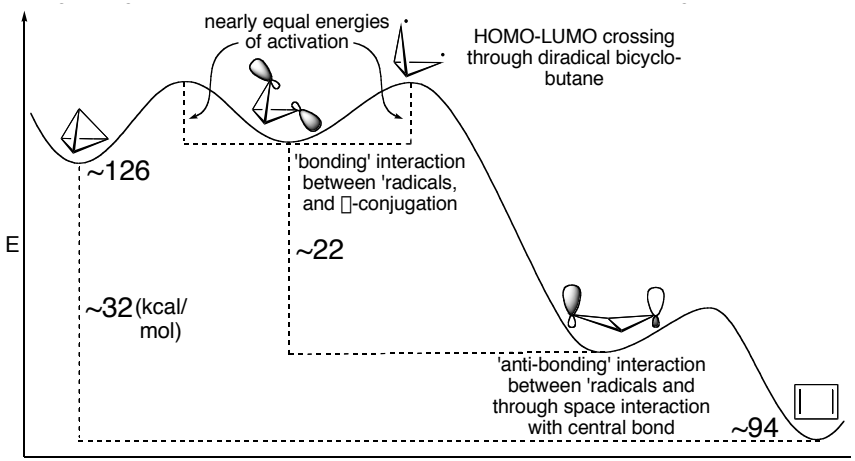

## *TETRAHEDRANE*

• Numerous attmpts towards its synthesis . . .



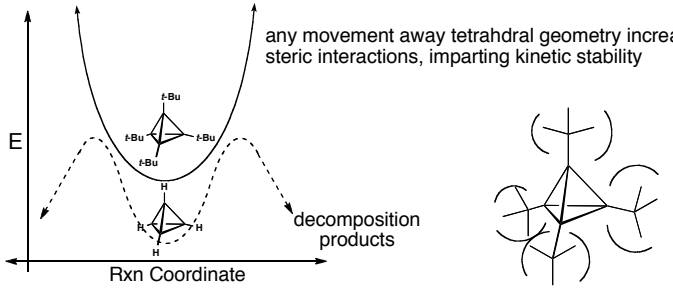

" . . . leaving as the only consolation the knowledge of how *not* to make tetrahedrane."
-Henning Hopf

• High-energy *diradical-like* intermediate can rapidly convert to its lower energy *lumomer*.




Schematic representation of the MERP (minimum energy reaction path) for conversion of tetrahedrane to cyclobutadiene.

• However, tetrahedrane ($E_{str}$= 126-140 kcal/mol) can be stabilized by 'corset effect.'

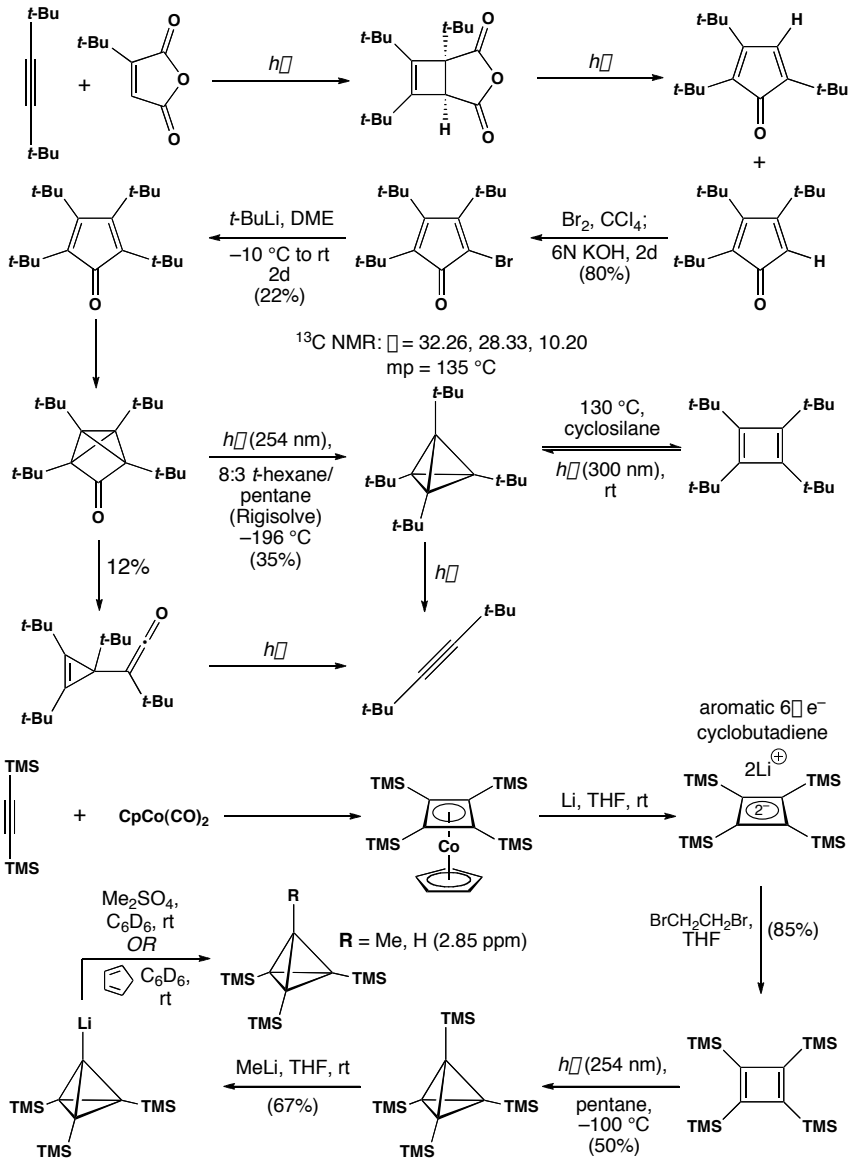



• Originally proposed and utilized by G. Maier *et al* in the first synthesis of a tetrahedrane

Maier, G. *et al Angew. Chem. Int. Ed. Engl.*, **1978**, 520.

# Platonic Hydrocarbons

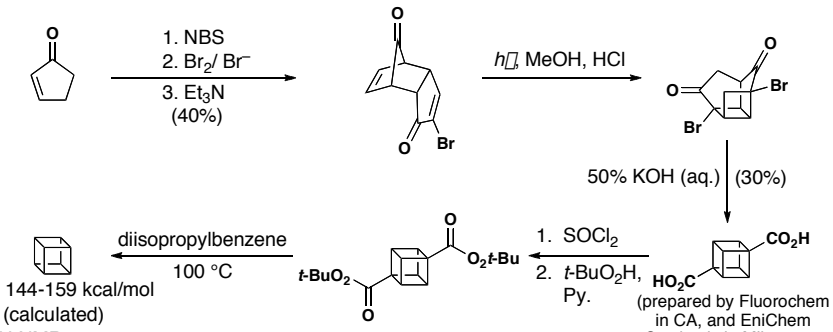




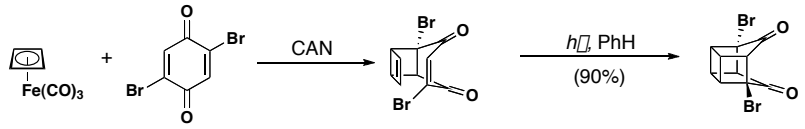

Sekiguchi, A. *et al. JACS*, **2003**, 12684.

## *Cubane (Hexahedrane)*

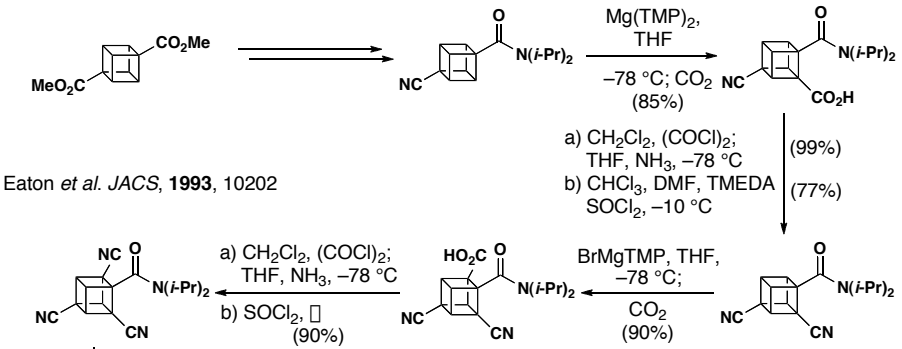
Eaton, P. E. *et al. JACS* **1964**, 962.
Eaton, P. E. *et al. JACS* **1964**, 3157.

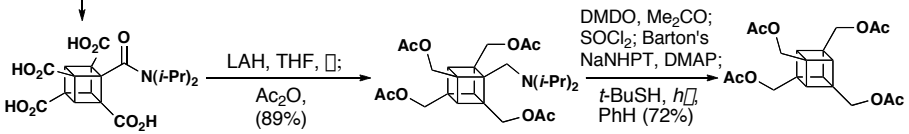



R. Pettit and co-workers *JACS* **1966**, 1328.



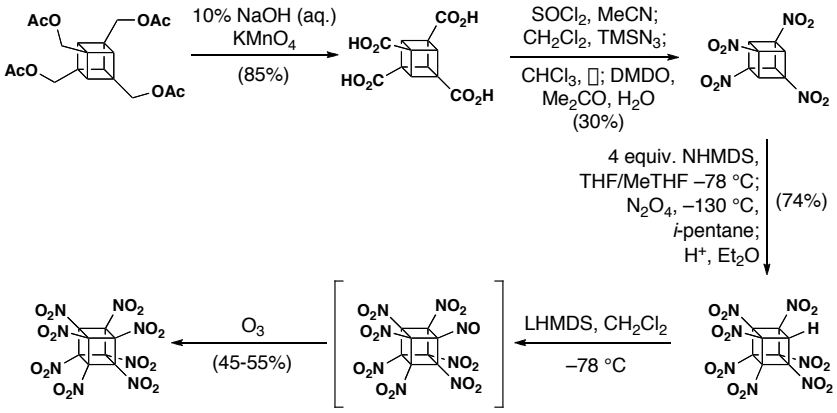

Eaton *et al. JACS*, **1993**, 10202



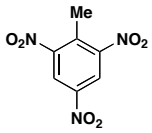



# Cubane

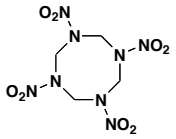




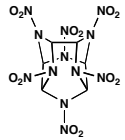

$\Delta H_f$ = 81-144 kcal/mol
density ~ 1,9-2.2 g/cm
'leads to calculated detonation velocities and pressures much higher than that of TNT, 15-30% greater than HMX and perhaps even better than CL-20, the most powerful nonnuclear explosive known.'



TNT



HMX



CL-20