Much Ado About Nothing: The Platonic Solids and Hydrocarbon Chemistry

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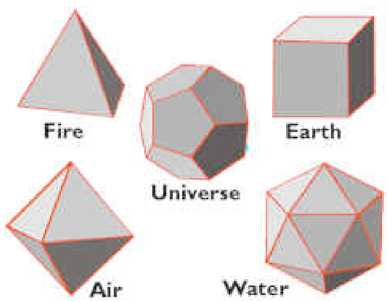
20th January 2004

Introduction - The Platonic Solids

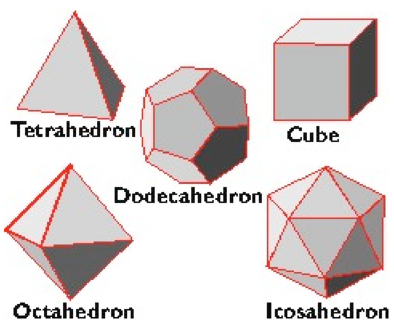


•According to Plato, the matter surrounding us and out of which we are made is composed of four elements: fire, earth, water and air.

•A fifth element also exists, not part of the physical world, but provides the basis for the construction of the "heavenly matter", or "ether", and is responsible for the "beautiful order" of the universe.

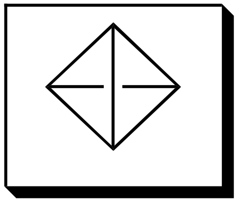
•These five elements are assigned characteristic regular polyhedra - the tetrahedron (fire), the cube (earth), the octahedron (water), the icosahedron (air) and the pentagonal dodecahedron (ether).

•These platonic solids are both pleasing aesthetically, and when considered as a hydrocarbon framework, provide interesting synthetic challenges.



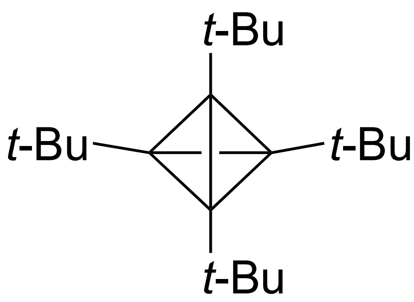
www.sbu.ac.uk/water/ platonic.html

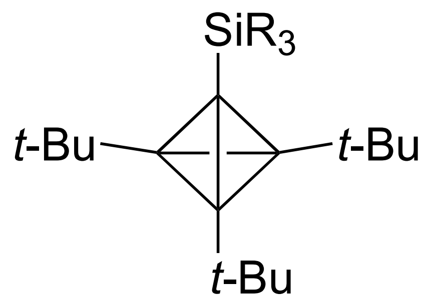
Tetrahedrane



- Tetrahedrane is the only platonic hydrocarbon which has not yet been prepared in unsubstituted form.
- 126-140 kcal/mol calculated strain energy, kinetically and thermodynamically highly unstable.

Tetra-*tert*-Butyl Tetrahedrane

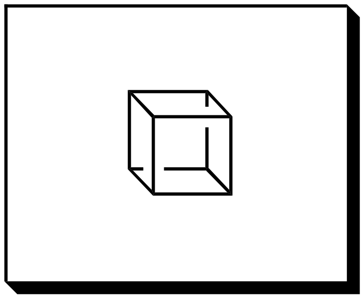




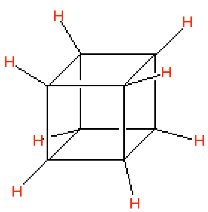
- The stability of tetra-tert-butyltetrahedrane compared to tetrahedrane is attributed to the ”corset effect”.
- Intramolecular repulsion between the four *tert*-butyl groups is at a minimum when their mutual distance is at a maximum. This condition is satisfied by the symmetry of a tetrahedron

G. Maier & S. Pfriem Angew. Chem. Int. Ed. Engl. (1978), *17*, 520

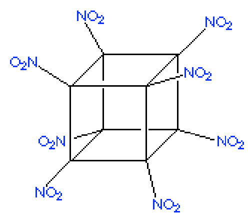
Cubane



Cubane, C_8H_8 was first synthesized by Eaton and Cole in 1964.



Cubane (C_8H_8)

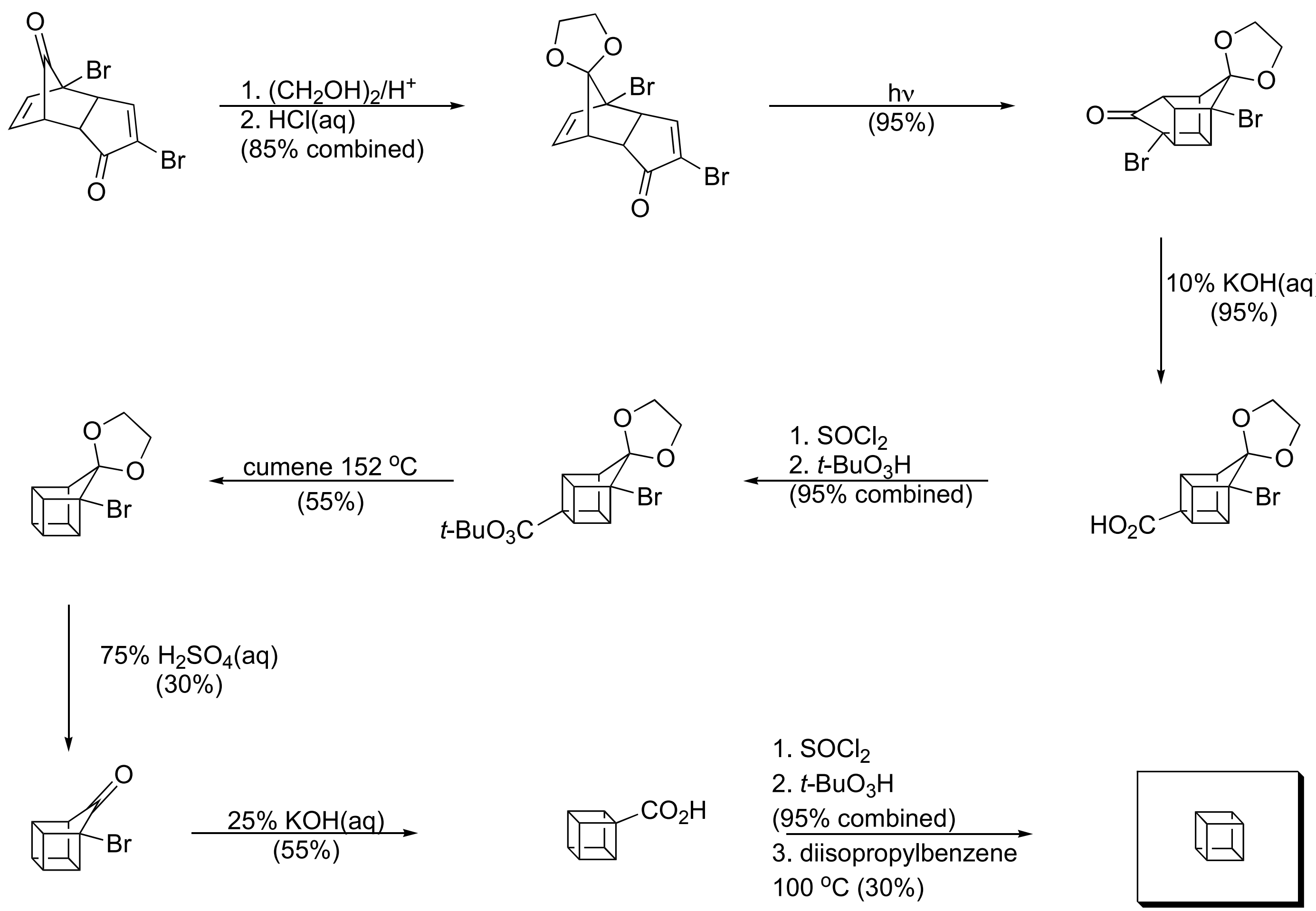


Octanitrocubane ($C_8N_8O_{16}$)

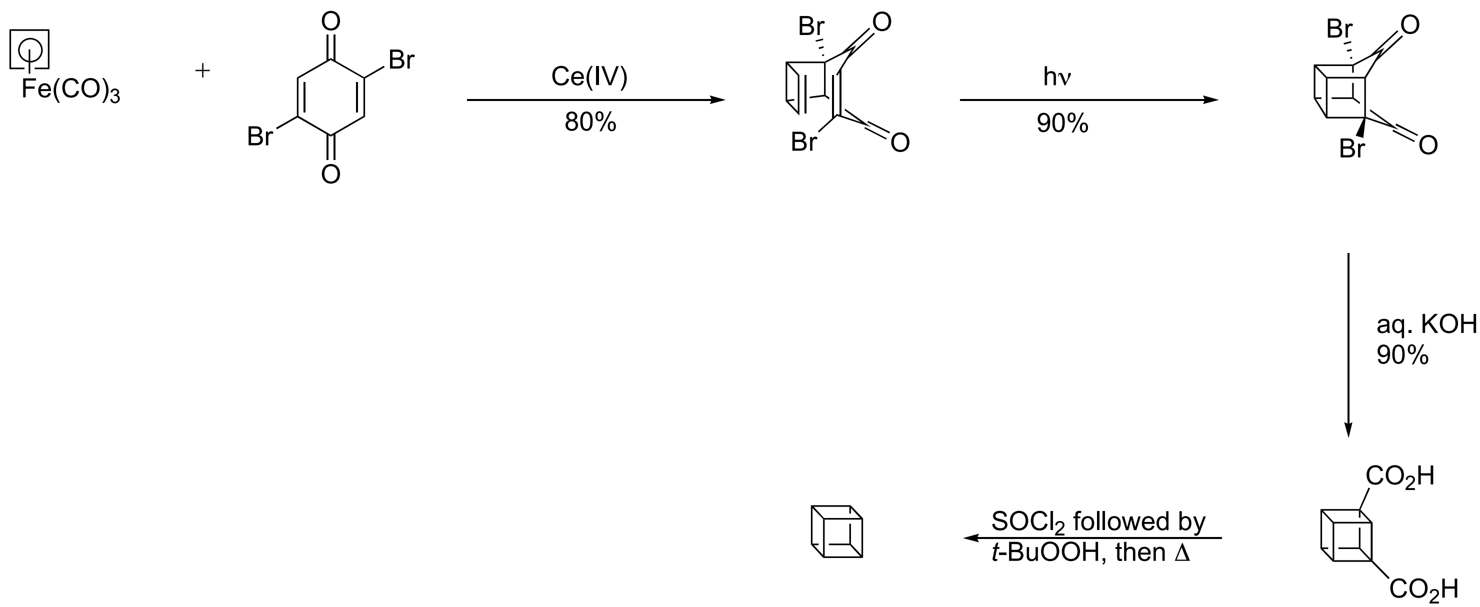
Octa- and other polynitrocubane derivatives
Have attracted considerable military interest,
The non-shock sensitive ONC is reported to be
30% more explosive than it's nearest non-nuclear alternative!

P.E. Eaton & T.W. Cole *J. Am. Chem. Soc.*, (1964), **86**, 962-964.
P.E. Eaton & T.W. Cole *ibid.*, (1964), **86**, 3157-3158.
P.E. Eaton *et al.Propellants, Explosives and Pyrotechnics*, (2002), **27**, 1-6.
P.E. Eaton *et al. Angew. Chemie. Int. Ed. Engl.*,(2000), **39**, 401-404.

Cubane - First Synthesis by Eaton and Cole

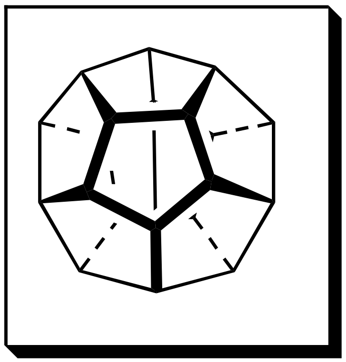


Cubane - An Alternative Synthesis by Pettit



R. Pettit, L. Watts & J. C. *J. Am. Chem. Soc.*, (1966), **88**, 1328-1329.

Dodecahedrane

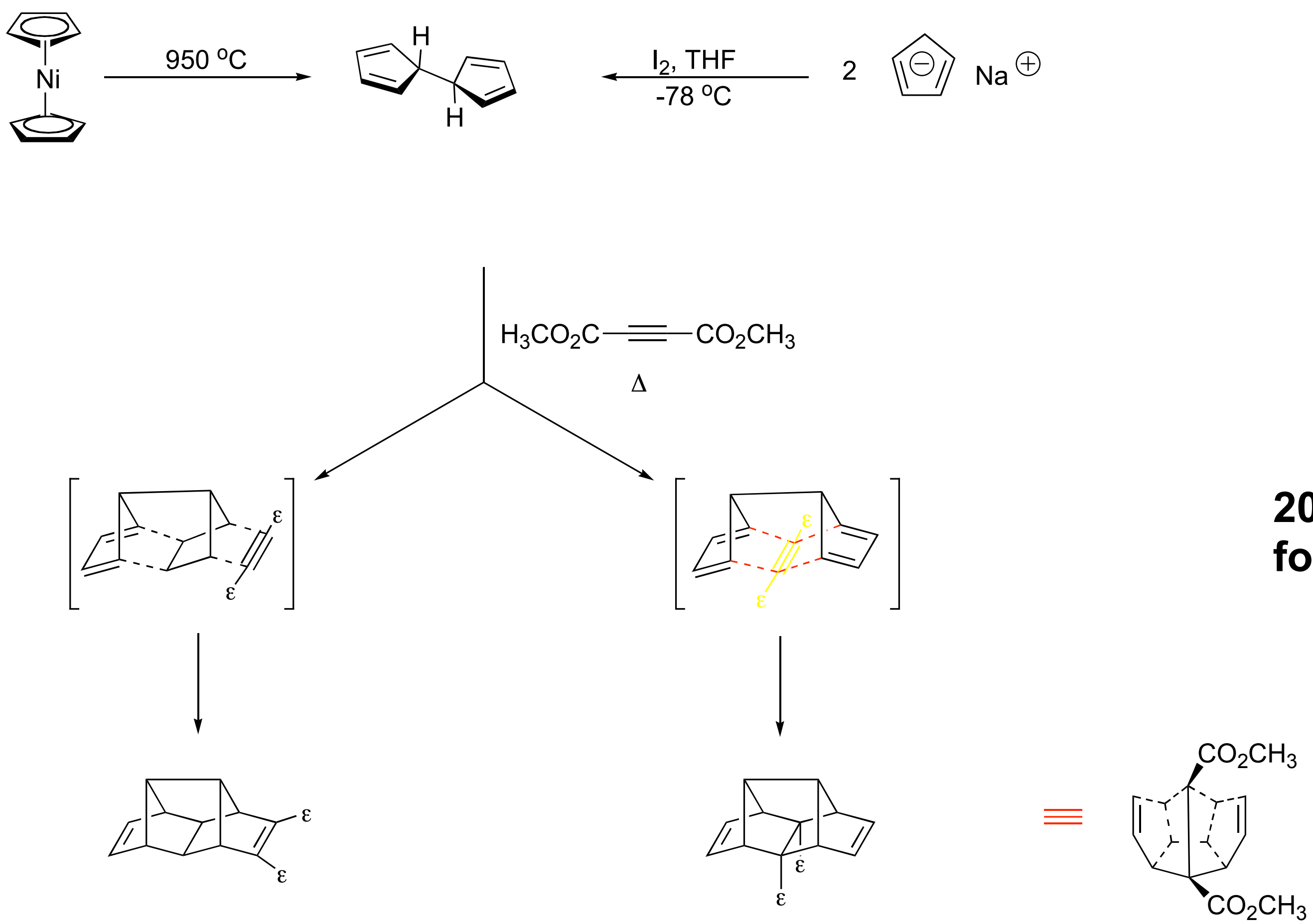


- The first dodecahedrane ever prepared was 1,16-dimethyl dodecahedrane in 19 steps in 1982 by Paquette and co-workers.

- Paquette reported the synthesis of the parent hydrocarbon by a similar route shortly afterwards.

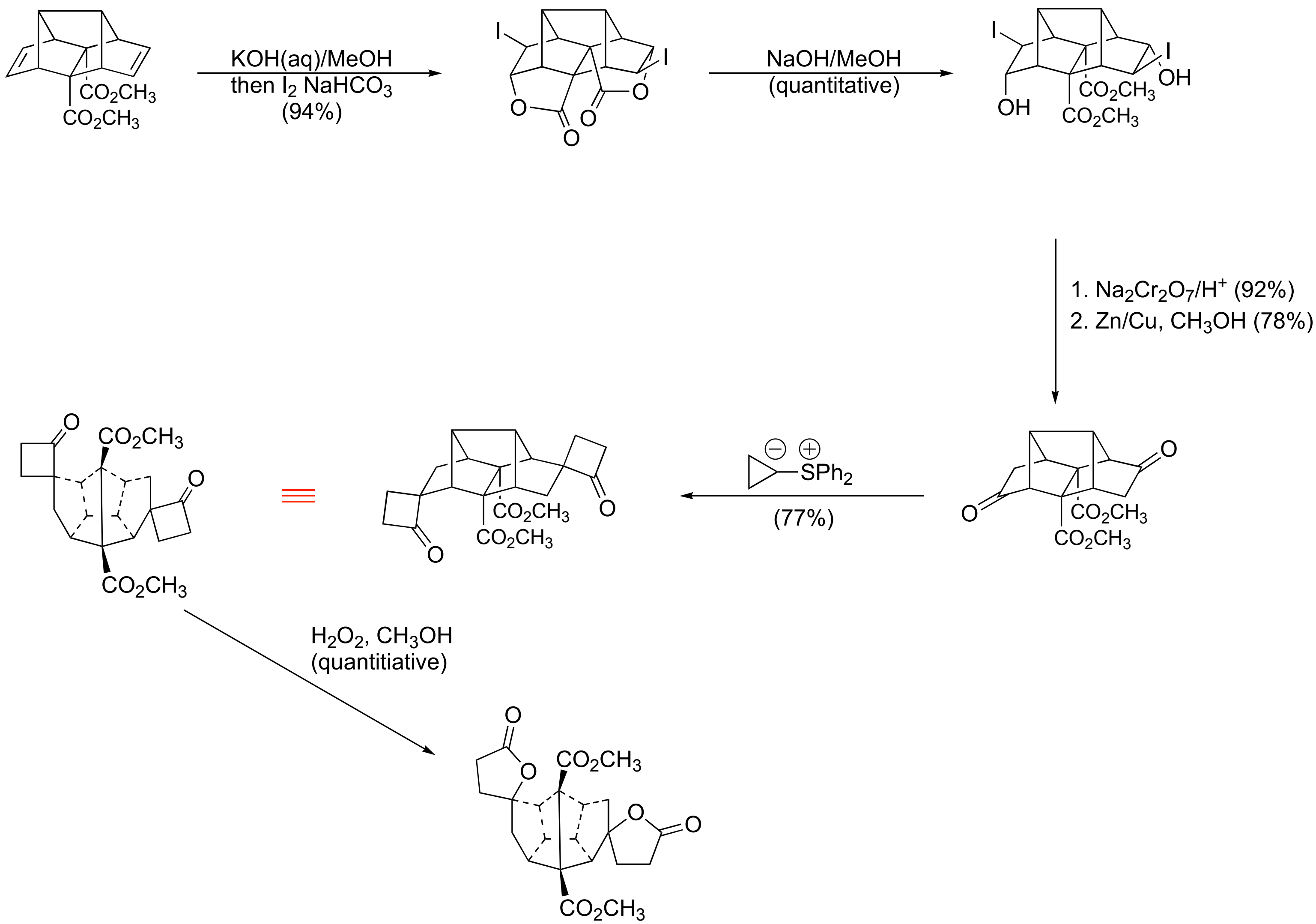
L.A. Paquette; D.W. Balogh & J.F. Blont *J. Am. Chem. Soc.*, (1981), *103*, 228-230.
L.A. Paquette; G.G. Christophe; D.W. Balogh, D. Kountz, R. Usha *Science* (1981), *211*, 575.
L.A. Paquette; D.W. Balogh *J. Am. Chem. Soc.*, (1982), *104*, 774-783.
L.A. Paquette; G.G. Christoph & D.W. Balogh, P.Engel, R. Usha *ibid*, (1982), *104*, 784-7.

Dodecahedrane - First Synthesis by Paquette

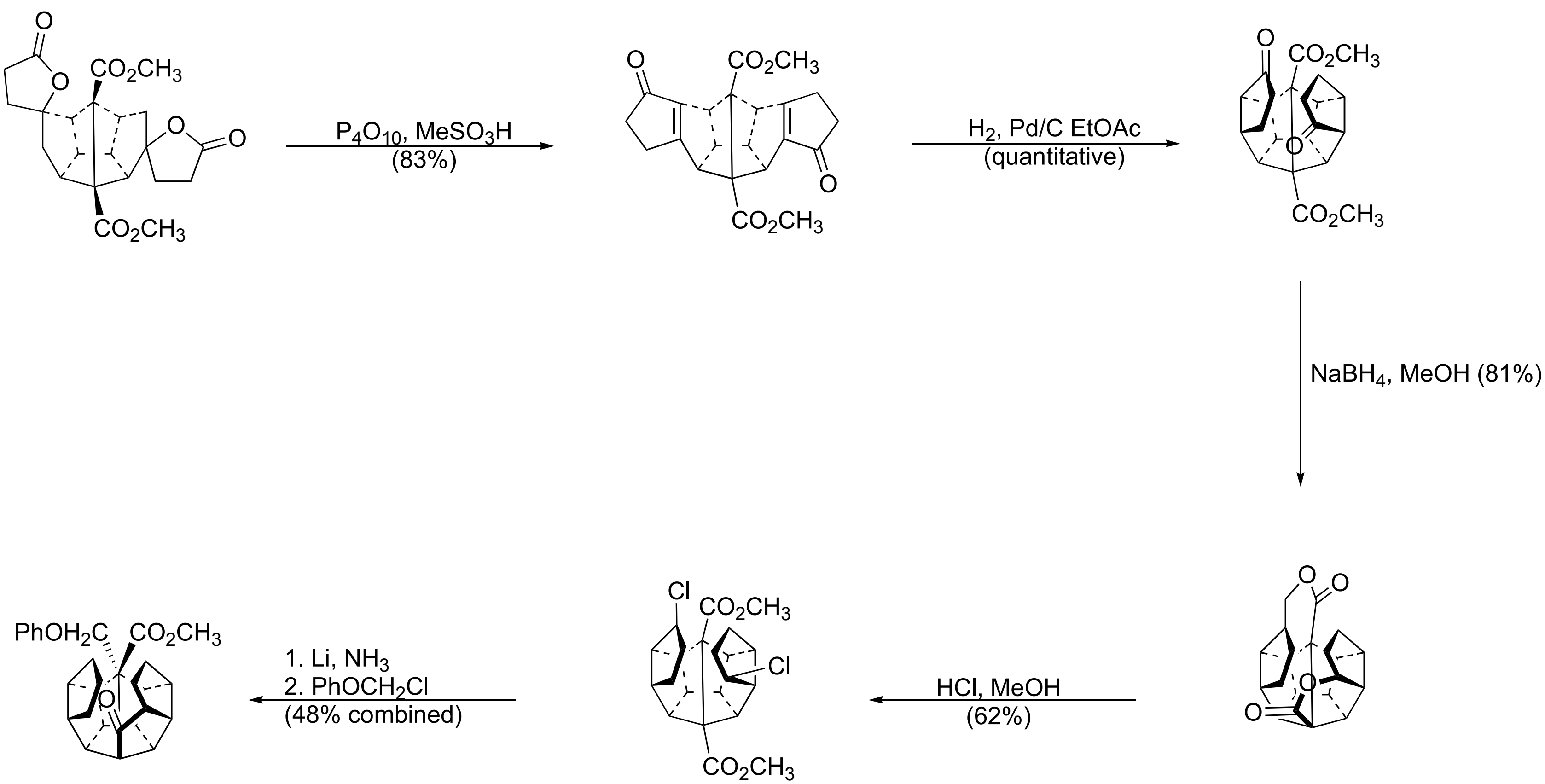


20% optimized yield for whole sequence

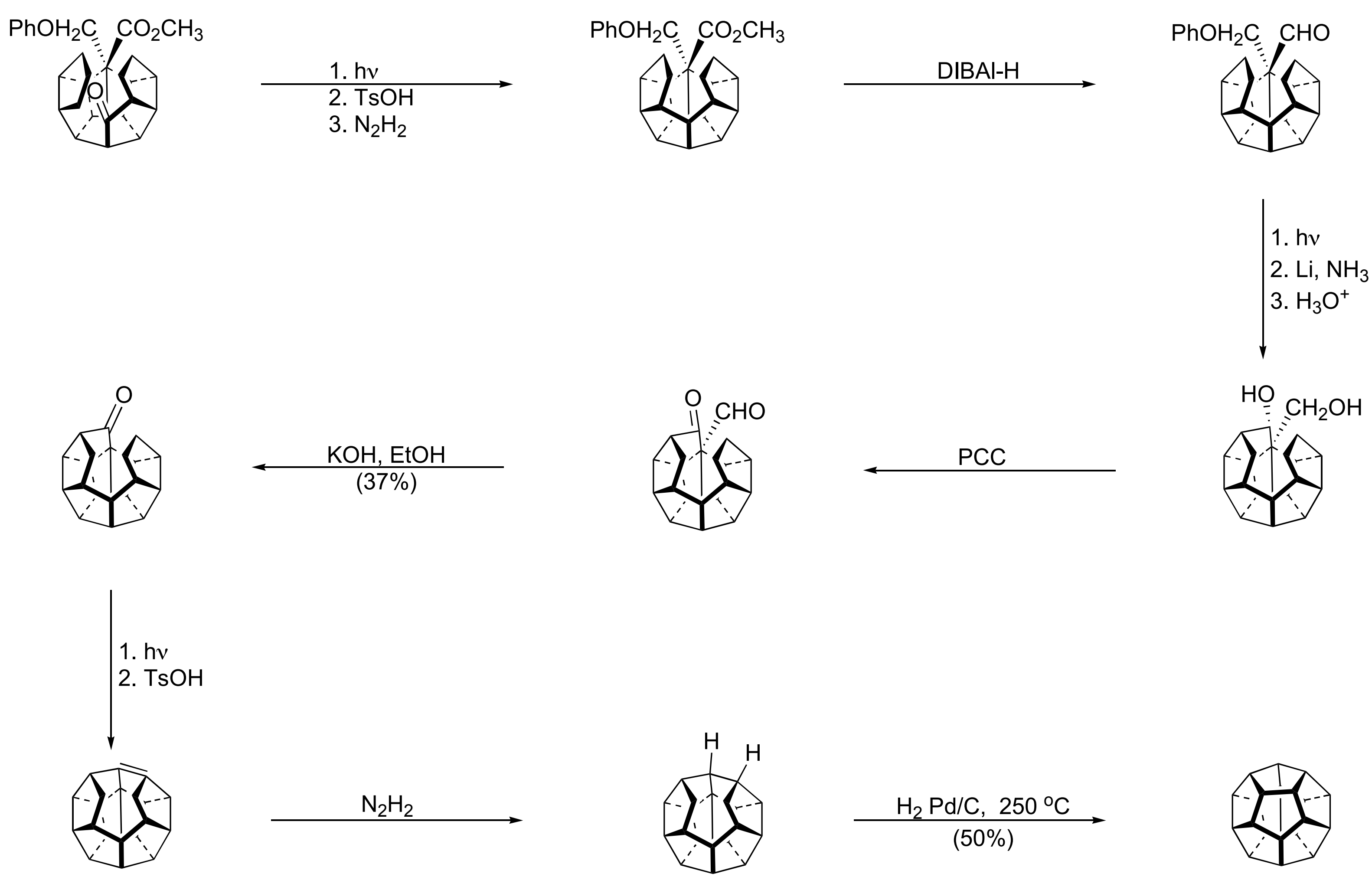
Completing the Carbon Framework



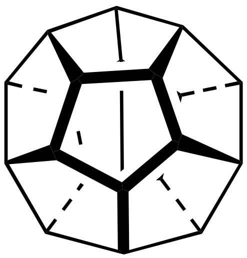
Closure of the Dodecahedrane Cage



Closure of the Dodecahedrane Cage



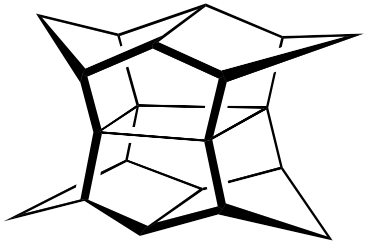
Dodecahedrane $C_{20}H_{20}$ Isomers



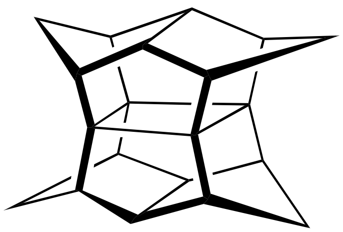
There are many $C_{20}H_{20}$ isomers, including various multi-bridged cyclophanes, dimers of C_{10} structures (e.g. basketene dimer) and other saturated polycyclic systems.

Interconversion of these hydrocarbons by thermally or photochemically mediated isomerization reactions has been the basis for several attempted syntheses of hydrocarbon structures.

Prinzbach and co-workers were able to demonstrate an alternative route to dodecahedrane, via the thermodynamically controlled isomerization of another $C_{20}H_{20}$ hydrocarbon, pagodane.



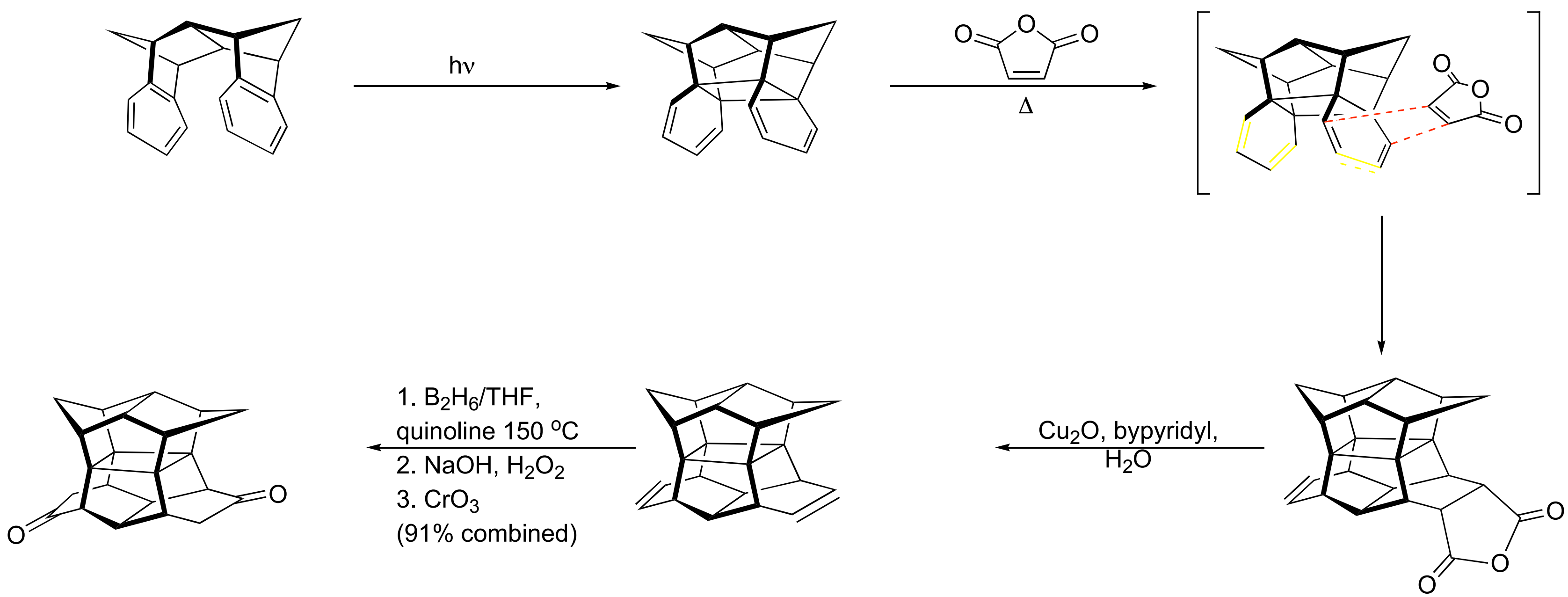
Pagodane



- *ca*. 40 kcal/mol higher heat of formation than dodecahedrane.
- Readily isomerized to dodecahedrane by Pt/Re on Al_2O_3.

W. D. Fessner; B. Murty; J. Worth; D. Hunkler; H. Fritz & H. Prinzbach
Angew. Chem. *Intl, Ed. Engl*., (1987), **26**, 452-454.

Building the Reflection of a Pagoda



Completion of the Carbon Framework