Much Ado About Nothing: The Platonic Solids and Hydrocarbon Chemistry

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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 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-\textit{\textit{tert}}-Butyl Tetrahedrane

- The stability of tetra-\textit{\textit{tert}}-butyltetrahedrane compared to tetrahedrane is attributed to the "corset effect".
- Intramolecular repulsion between the four \textit{\textit{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

Cubane

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

Octa- and other polynitrocubane derivatives have attracted considerable military interest. The non-shock sensitive ONC is reported to be 30% more explosive than its nearest non-nuclear alternative!

Cubane - First Synthesis by Eaton and Cole

1. (CH₂OH)₂/H⁺
   2. HCl(aq)
      (85% combined)

   1. SOCl₂
      2. t-BuO₃H
         (95% combined)

   1. (CH₂OH)₂/H⁺
      2. HCl(aq)
          (85% combined)

   10% KOH(aq)
       (95%)

   75% H₂SO₄(aq)
       (30%)

   25% KOH(aq)
       (55%)

   1. SOCl₂
      2. t-BuO₃H
         (95% combined)
      3. diisopropylbenzene
         100 °C (30%)

   cumene 152 °C
       (55%)

   t-BuO₃C

   HO₂C
Cubane - An Alternative Synthesis by Pettit

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.

**Dodecahedrane - First Synthesis by Paquette**

\[
\text{Ni} \quad 950 \, ^\circ \text{C} \quad \text{H}_3\text{C}O\text{C} \quad \Gamma, \text{THF} \quad -78 \, ^\circ \text{C} \quad 2 \quad \text{Na}^+ \\
\]

\[
\Delta \\
\]

20% optimized yield for whole sequence
Completing the Carbon Framework

[Chemical structures and reactions]

1. Na$_2$Cr$_2$O$_7$/H$^+$ (92%)
2. Zn/Cu, CH$_3$OH (78%)

H$_2$O$_2$, CH$_3$OH (quantitative)
Closure of the Dodecahedrane Cage

1. **Closure with**
   - **P₄O₁₀, MeSO₃H (83%)**
   - **H₂, Pd/C EtOAc (quantitative)**
   - **NaBH₄, MeOH (81%)**

2. **Additional steps**
   - 1. **Li, NH₃ (48% combined)**
   - 2. **PhOCH₂Cl**
   - **HCl, MeOH (62%)**
Closure of the Dodecahedrane Cage

PhOH₂C₅CO₂CH₃ ➔ 1. hv
2. TsOH
3. N₂H₂

PhOH₂C₅CO₂CH₃ ➔ DIBAI-H ➔ PhOH₂C₅CHO

PhOH₂C₅CHO ➔ KOH, EtOH
(37%)

PhOH₂C₅CHO ➔ PCC ➔ HOCH₂OH

PhOH₂C₅CHO ➔ 1. hv
2. Li, NH₃
3. H₃O⁺

PhOH₂C₅CHO ➔ 1. hv
2. TsOH

PhOH₂C₅CHO ➔ N₂H₂ ➔ H₂Pd/C, 250 °C
(50%)
Dodecahedrane $\text{C}_{20}\text{H}_{20}$ Isomers

There are many $\text{C}_{20}\text{H}_{20}$ isomers, including various multi-bridged cyclophanes, dimers of $\text{C}_{10}$ 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 $\text{C}_{20}\text{H}_{20}$ hydrocarbon, pagodane.
Pagodane

• ca. 40 kcal/mol higher heat of formation than dodecahedrane.
• Readily isomerized to dodecahedrane by Pt/Re on Al₂O₃.

W. D. Fessner; B. Murty; J. Worth; D. Hunkler; H. Fritz & H. Prinzbach
Building the Reflection of a Pagoda

1. $\text{B}_2\text{H}_6/\text{THF}$, quinoline 150 °C
2. $\text{NaOH}, \text{H}_2\text{O}_2$
3. $\text{CrO}_3$
(91% combined)
Completion of the Carbon Framework

1. HCO$_2$CH$_3$/NaH
2. p-TsN$_3$/NEt$_3$ rt
(82% combined)

MeOH hv, rt
(95%)

Na-K, THF, then t-BuOH
(quantitative)

Pb(OAc)$_4$, I$_2$, CCl$_4$, hv
(80%)

H$_3$CO$_2$C

CO$_2$CH$_3$