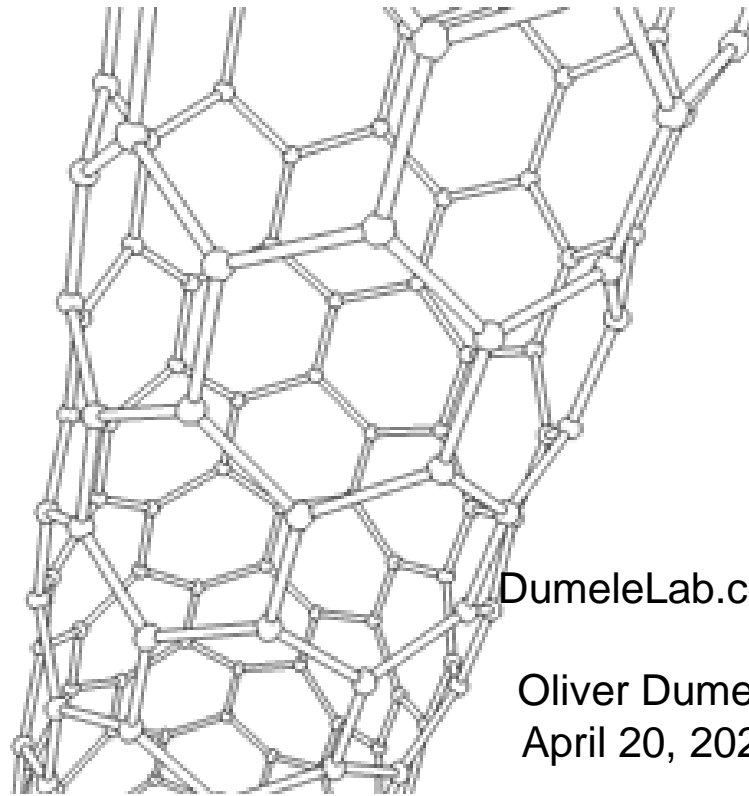


Lawrence T. Scott



DumeleLab.com

Oliver Dumele
April 20, 2020

Born 1944 (Ann Arbor, MI) — grew up in Urbana, IL

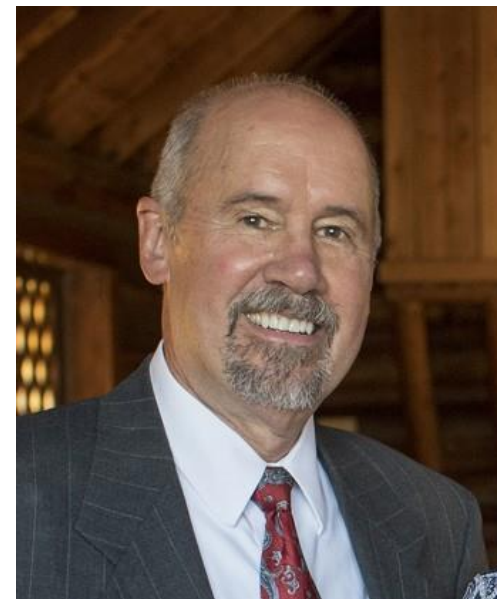
- 1966: Undergraduate Studies (A.B. degree), Princeton (with Prof. M. Jones)
- 1966–1970: PhD in Organic Chemistry, Harvard (with Prof. R. B. Woodward)
- 1970–1975: Assistant Professor, UCLA
- 1975–1993: (Associate) Professor, University of Nevada, Reno
- 1993–2019: Professor of Chemistry, Boston College

- since 2019: Professor of Chemistry Emeritus at Boston College

- Over 254 peer-reviewed publications (Scopus, 2020)

- H-index 59

- Cope Scholar Award, 2016
- George A. Olah Award for Hydrocarbon Chemistry, 2011
- *JOC* – Editorial Advisory Board, 2011–2014
- Gordon Research Conference on Physical Organic Chemistry – Chairman, 2003
- Alexander von Humboldt Foundation – Senior Scientist Award, 1999



Undergraduate Work (1965–1966): (CH)₁₀ era

“His [Scott’s] lifelong passion for highly unsaturated polycyclic hydrocarbons arose from his undergraduate thesis project on bullvalene and related (CH)₁₀ compounds in the laboratory of Prof. Maitland Jones, Jr. at Princeton University.”

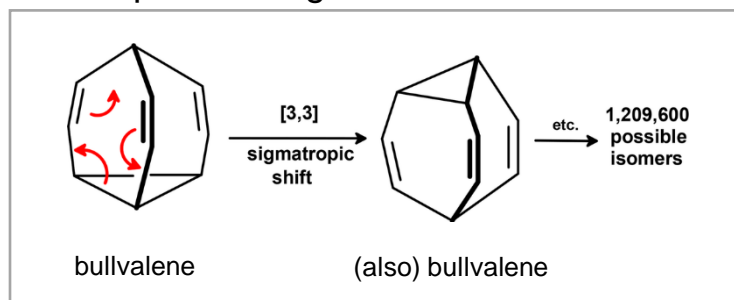
comment written by L. T. Scott
Angew. Chem. Int. Ed. **2004**, 73, 4994



Maitland Jones, Jr.,
*1937

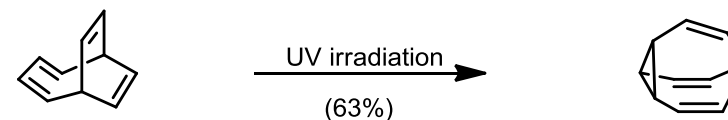
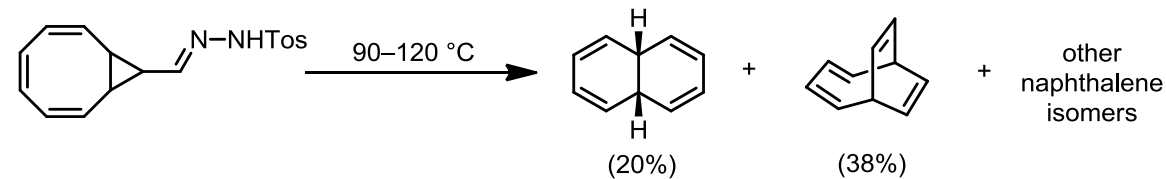
Reminder:

Cope rearrangements of Bullvalene



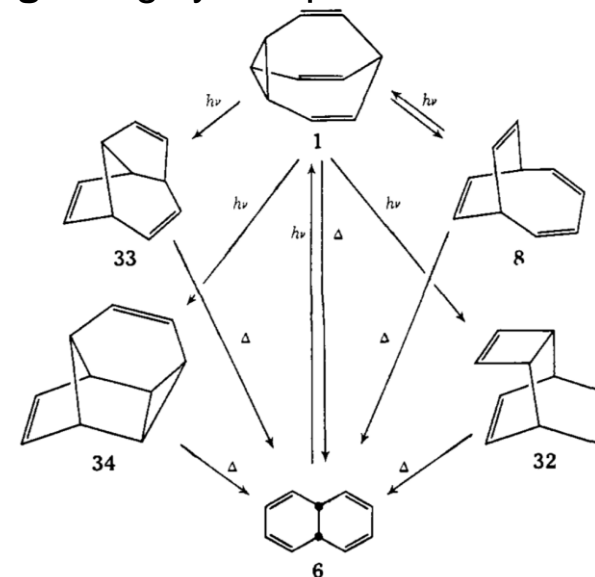
W. von E. Doering, W. Roth *Tetrahedron* **1963**, 19, 715

early work on C₁₀H₁₀ scaffolds (thermal and photo reactions)



M. Jones, Jr., L. T. Scott *J. Am. Chem. Soc.* **1967**, 89, 150

early understanding of highly complex carbon scaffold transformations



M. Jones, Jr., S. D. Reich, L. T. Scott *J. Am. Chem. Soc.* **1970**, 92, 3118

PhD Work (1966–1970)

with Robert B. Woodward (Harvard)



no single paper published of his PhD work with Woodward

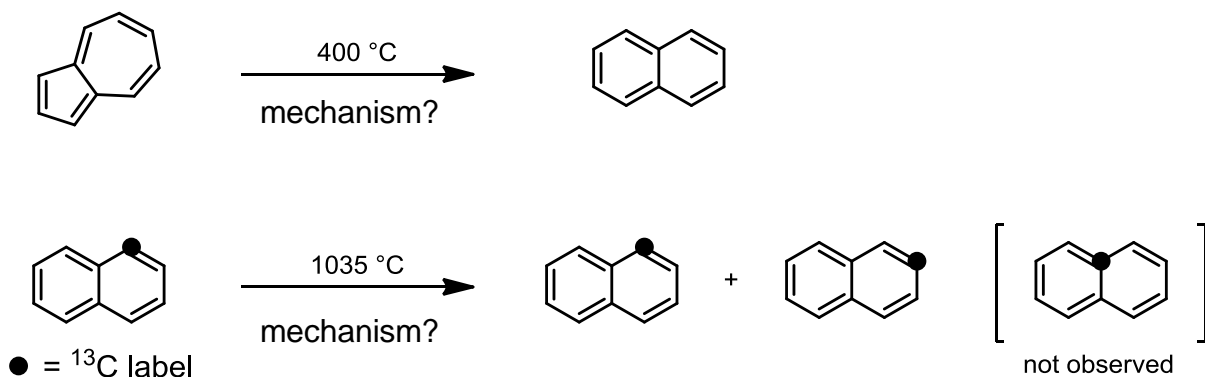
but

- 1) wrote a very comprehensive review about the field of his undergraduate work:

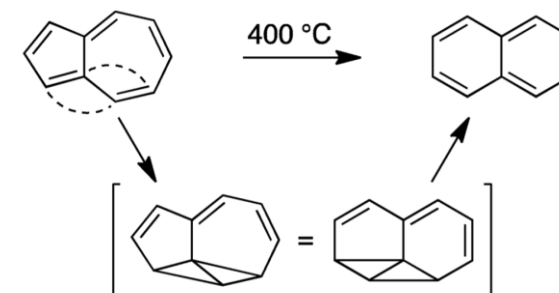
“Rearrangements and interconversions of compounds of the formula $(CH)_n$ ” L. T. Scott, M. Jones, Jr. *Chem. Rev.* **1972**, *72*, 181

- 2) observed the era of Woodward when he wrote the famous book “*The Conservation of Orbital Symmetry*” together with R. Hoffmann

- 3) impressed Woodward with a proposal of the mechanism for an **azulene–naphthalene** isomerization (*J. Org. Chem.* **2016**, *81*, 11535).



Scott's proposal (accepted by Woodward):



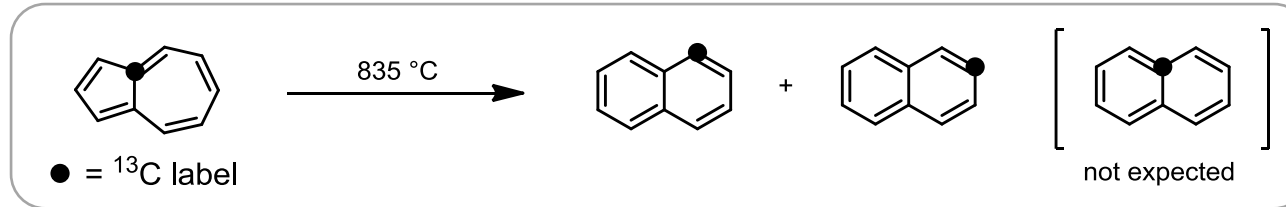
→ despite many attempts, never proven correct

Independent work (starting in 1970): Wanted to change direction and branch out, but:

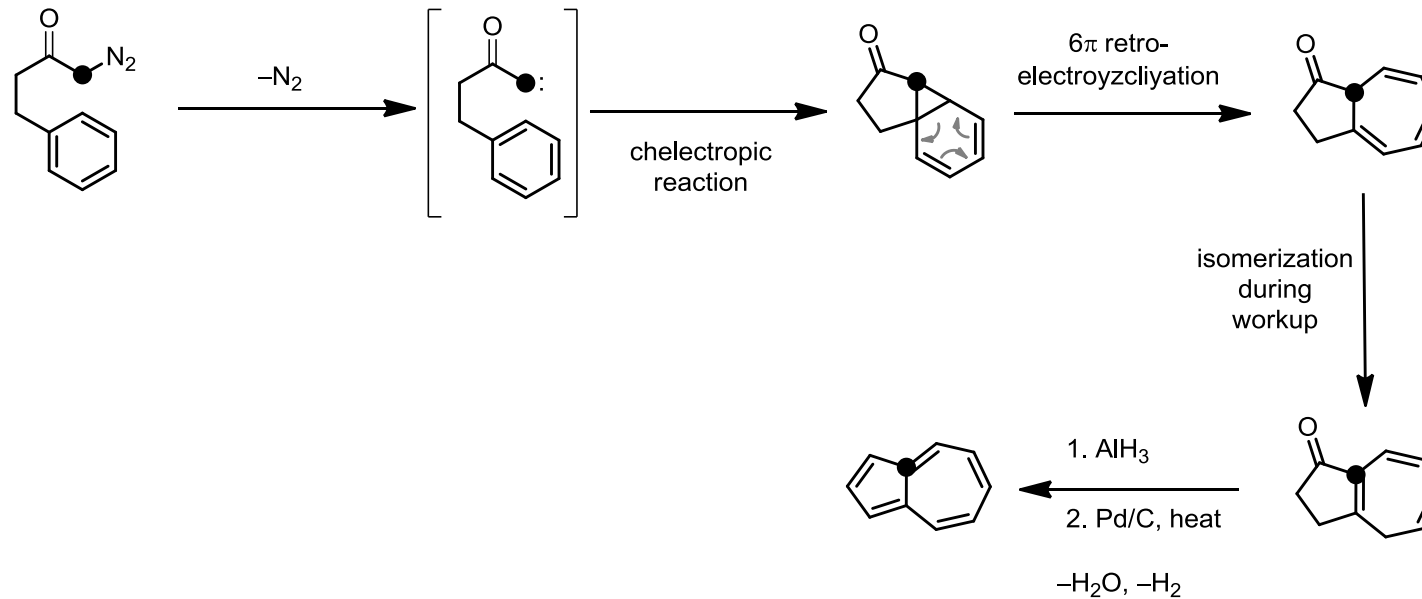
“Nevertheless, I was unable to resist the urge to tackle the azulene-to-naphthalene rearrangement problem myself in the laboratory.”

L. T. Scott *J. Org. Chem.* **2016**, *81*, 11535

proposed control experiment:

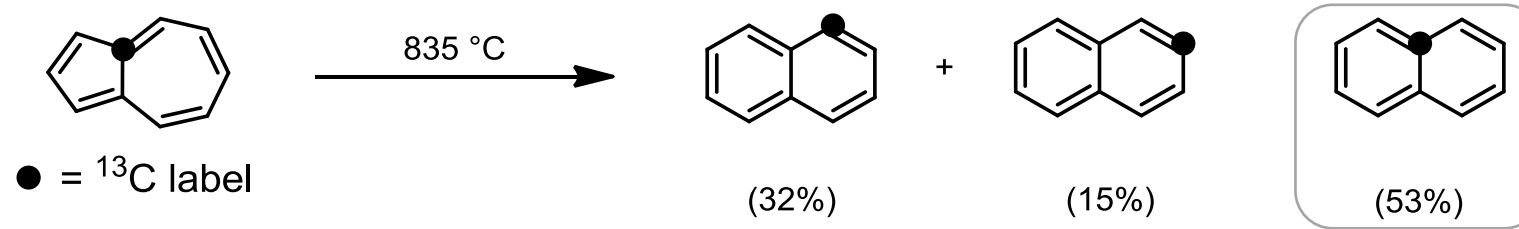


Developed the shortest azulene synthesis known until then



L. T. Scott, M. A. Minton, M. A. Kirms *J. Am. Chem. Soc.* **1980**, *102*, 6311

Result of the key azulene labeling experiment:



unexpected product formed!
→ **proposed mechanism is wrong!**

“Our confidence in our understanding of the thermal behavior of azulene and naphthalene was instantly shattered”

The mechanism remains unsolved until today

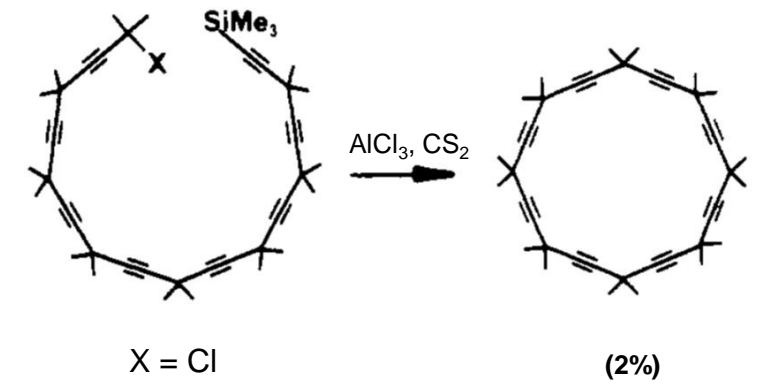
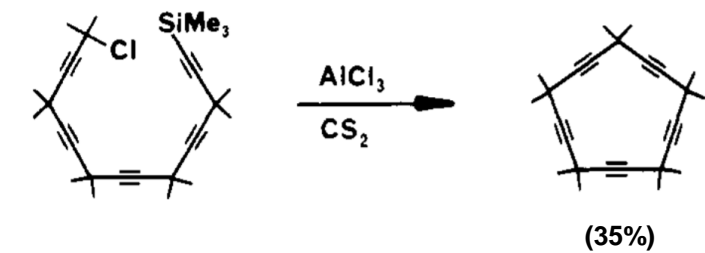
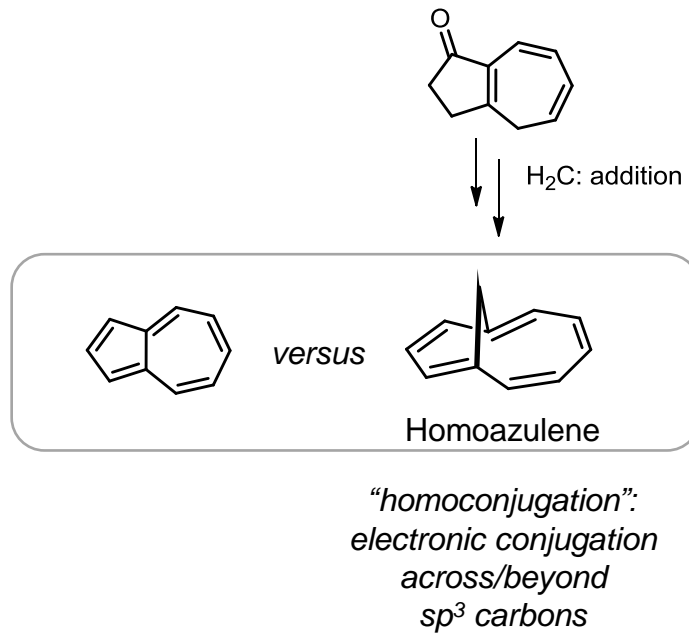
Scott, L. T. *J. Org. Chem.* **2016**, *81*, 11535

mid 80s: cyclic olefinic/aromatic hydrocarbons

AND

acetylene chemistry

“Cyclynes”



L. T. Scott, W. R. Brunsvold, M. A. Kirms, I. Erden
J. Am. Chem. Soc. **1981**, *103*, 5216

L. T. Scott, G. J. DeCicco, J. L. Hyun, G. Reinhardt *J. Am. Chem. Soc.* **1985**, *107*, 6546

mid 90s: Fullerenes and carbon nanotubes were discovered: H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162

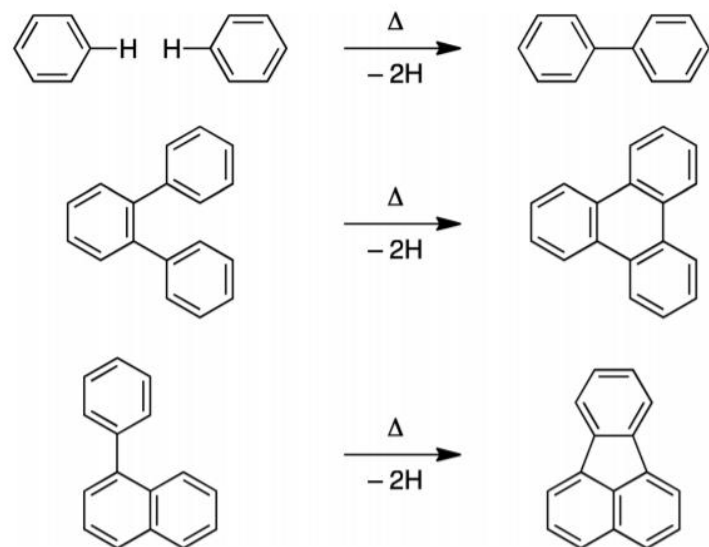
“When I first heard that C_{60} had been detected in fuel-rich flames, I was stunned.”

J. B. Howard, J. T. McKinnon, Y. Makarovsky, A. L. Lafleur, M. E. Johnson, *Nature* **1991**, *352*, 139

L. T. Scott *J. Org. Chem.* **2016**, *81*, 11535

→ motivation to synthesize these carbon allotropes “bottom up”

What was known?

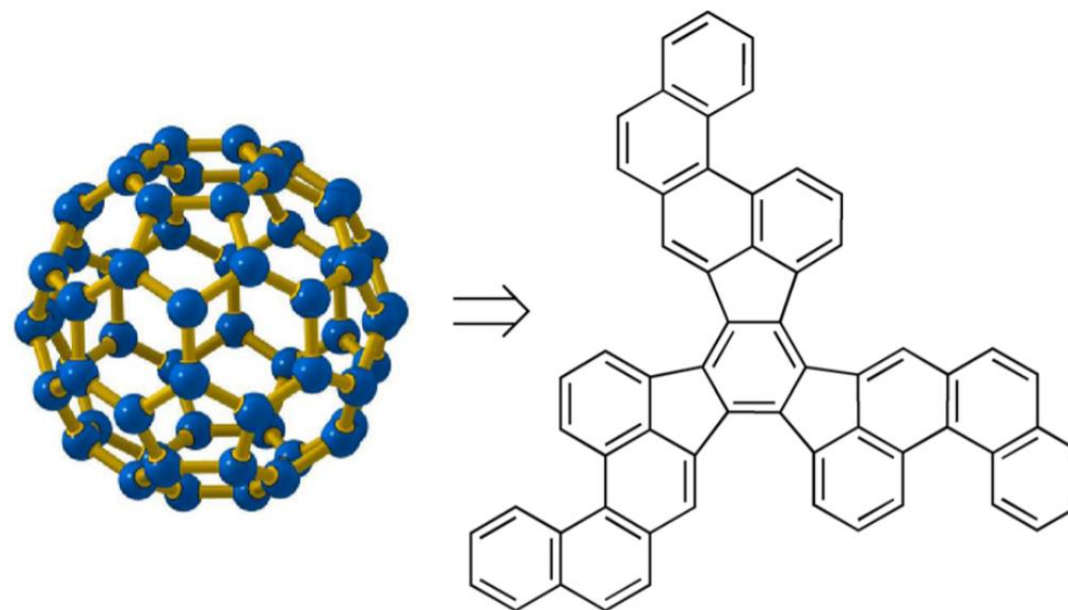


M. Berthelot *Z. Chem.* **1866**, 707

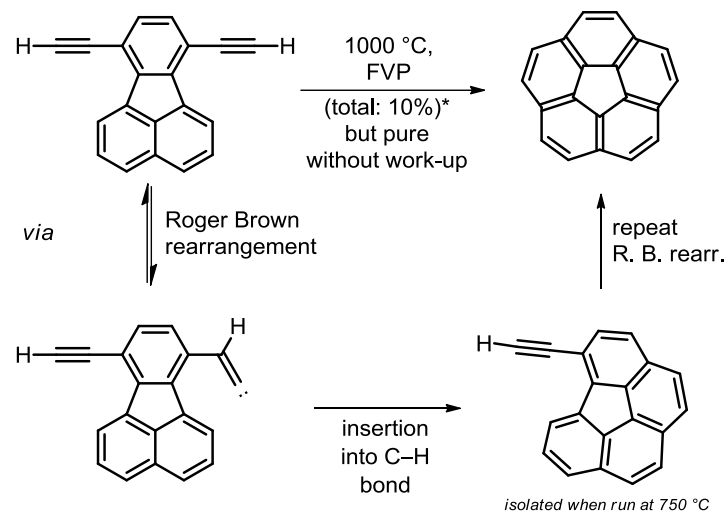
C. Jacobelli, G. Perez, C. Polcaro, E. Possagno, R. Bassanelli, E. Lilla
J. Anal. Appl. Pyrolysis **1983**, *5*, 237

M. Orchin, L. Reggel *J. Am. Chem. Soc.* **1947**, *69*, 505

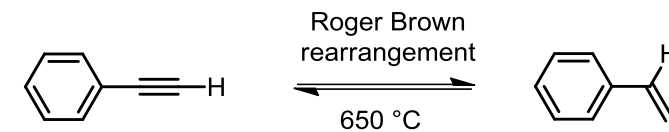
Scott's proposal: pyrolysis of a designed precursor



First “training targets” towards Fullerene: **Corannulene**



Scott was inspired by and designed it based on the (infamous) Roger Brown rearrangement:

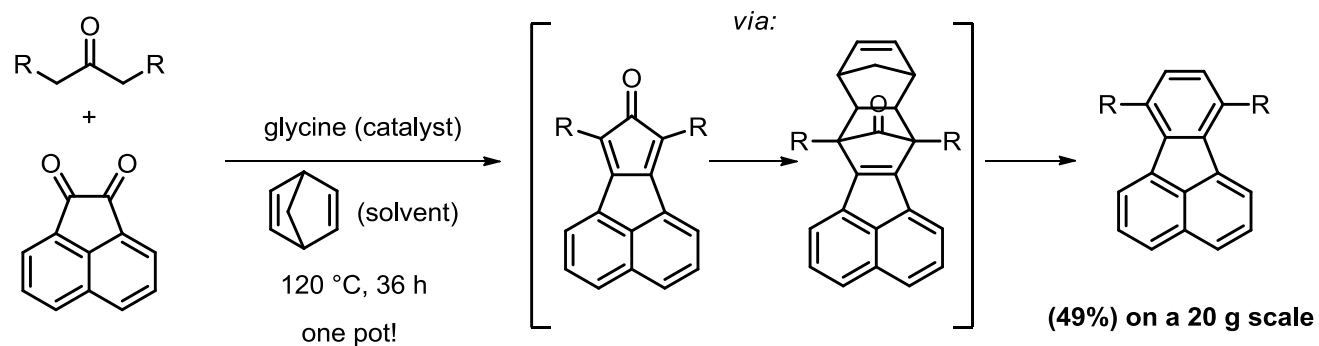


R. F. C. Brown, K. J. Harrington, G. L. J. McMullen
Chem. Soc., Chem. Commun. **1974**, 123–124.

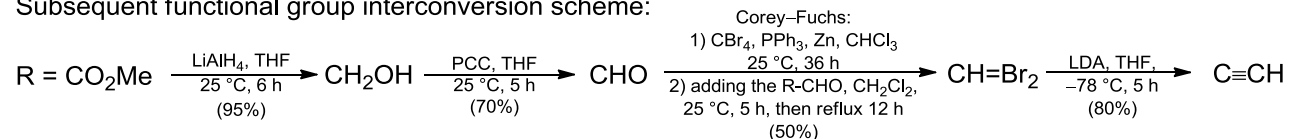
L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. J. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082

The Scott lab had to develop a new and simpler one-pot procedure for the precursor:

[→ note: similar method as K. Müllen makes cyclopentadienone precursors for the Diels–Alder reaction with acetylenes]



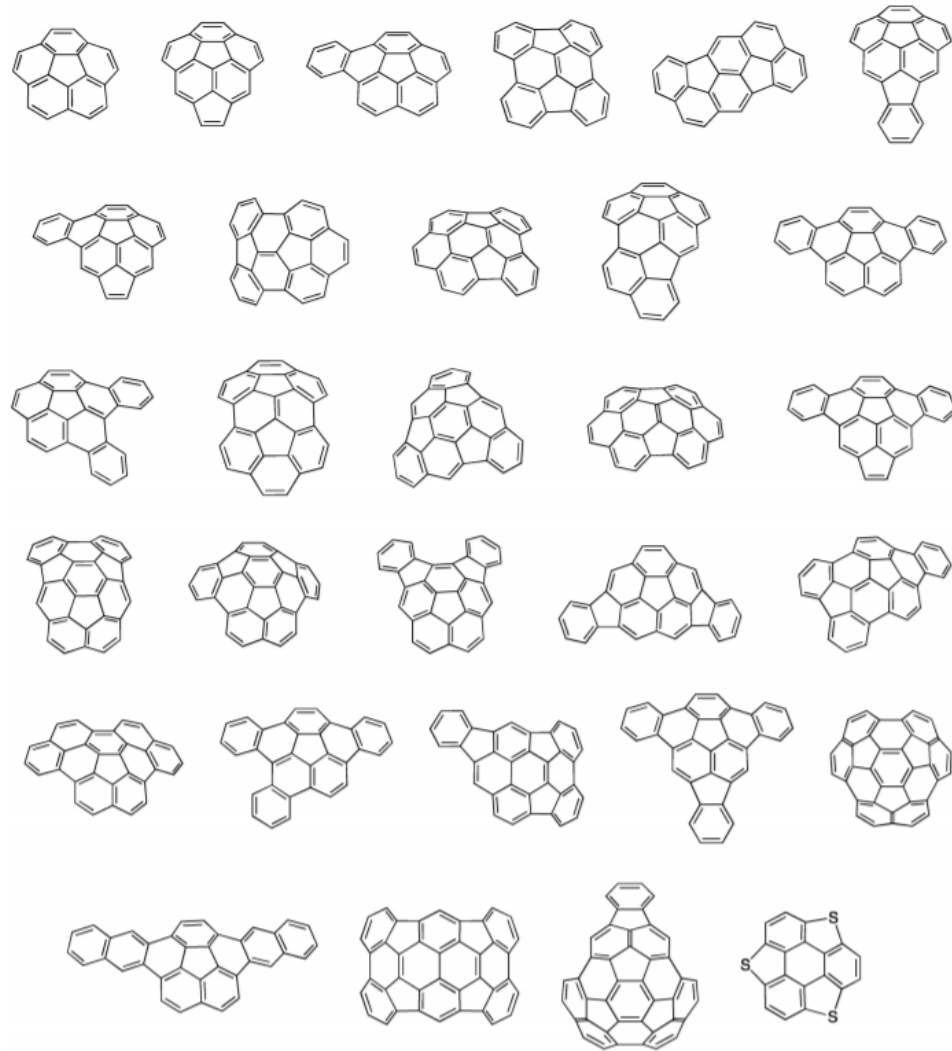
Subsequent functional group interconversion scheme:



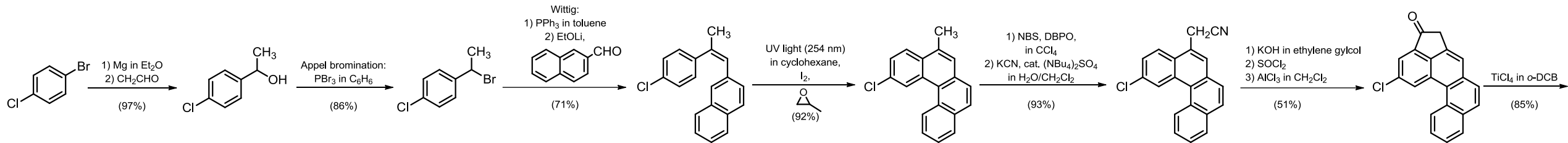
→ same JACS paper as above

towards Fullerene: Geodesic Hydrocarbons

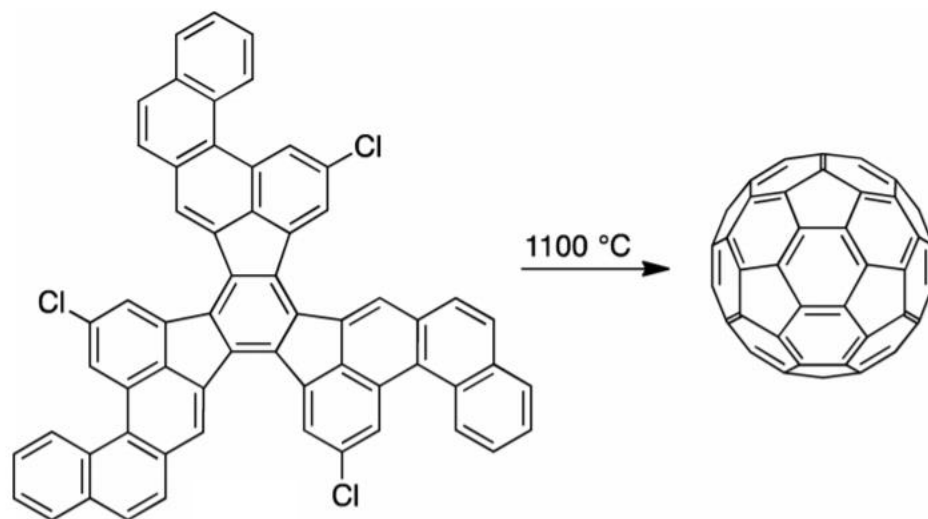
**Observed products in various Flash Vacuum Pyrolysis → New terminology:
“Geodesic Hydrocarbons”**



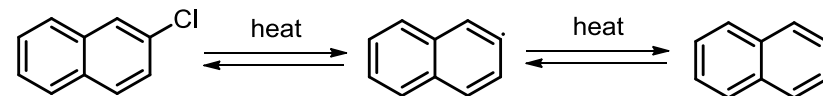
Finally Fullerene: Installation of chlorine achieved milligram quantities in Flash Vacuum Pyrolysis



first bottom-up synthesis of C₆₀ fullerene



- first in the gas phase in mass spectrometer, but without Cl substitution.
- one year later: with Cl, mg-scale by FVP → yield around 2%.
- Cl thermo-hemolytic cleavage forms radical, that can swap with it's adjacent C–H:



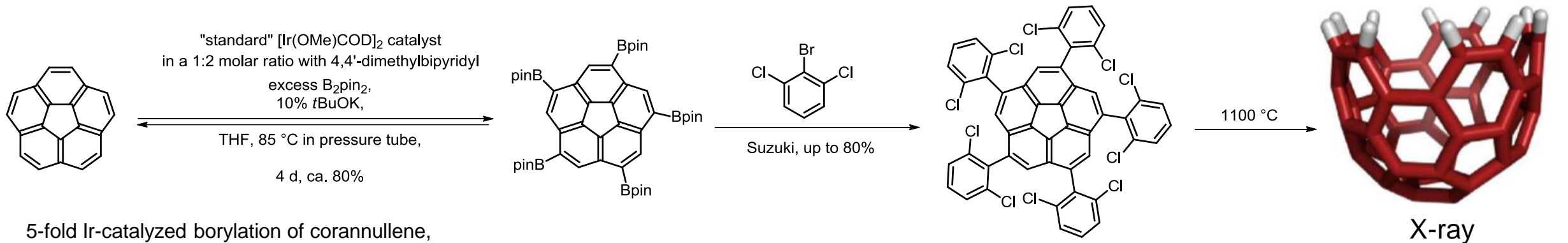
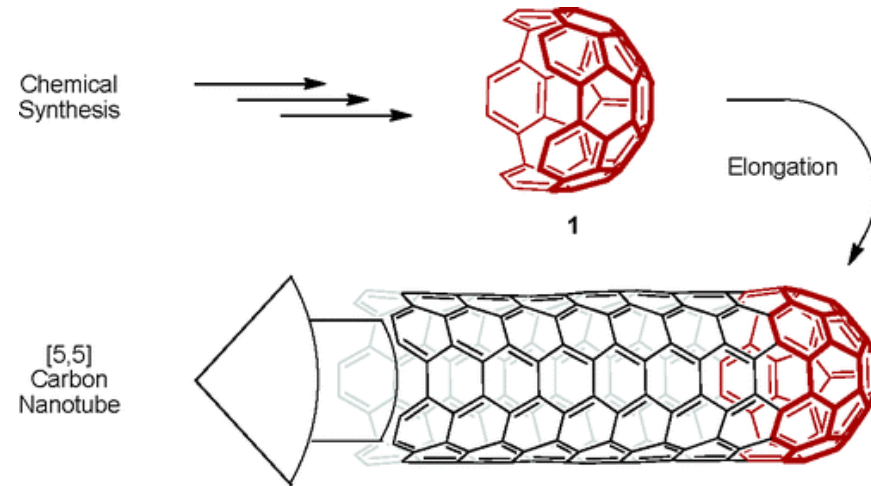
(also found by Scott, see in the ref. below)

M. M. Boorum, Y. V. Vasilev, T. Drewello, L. T. Scott *Science* **2001**, *294*, 828

L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere *Science* **2002**, *295*, 1500

Next: Nanotube synthesis

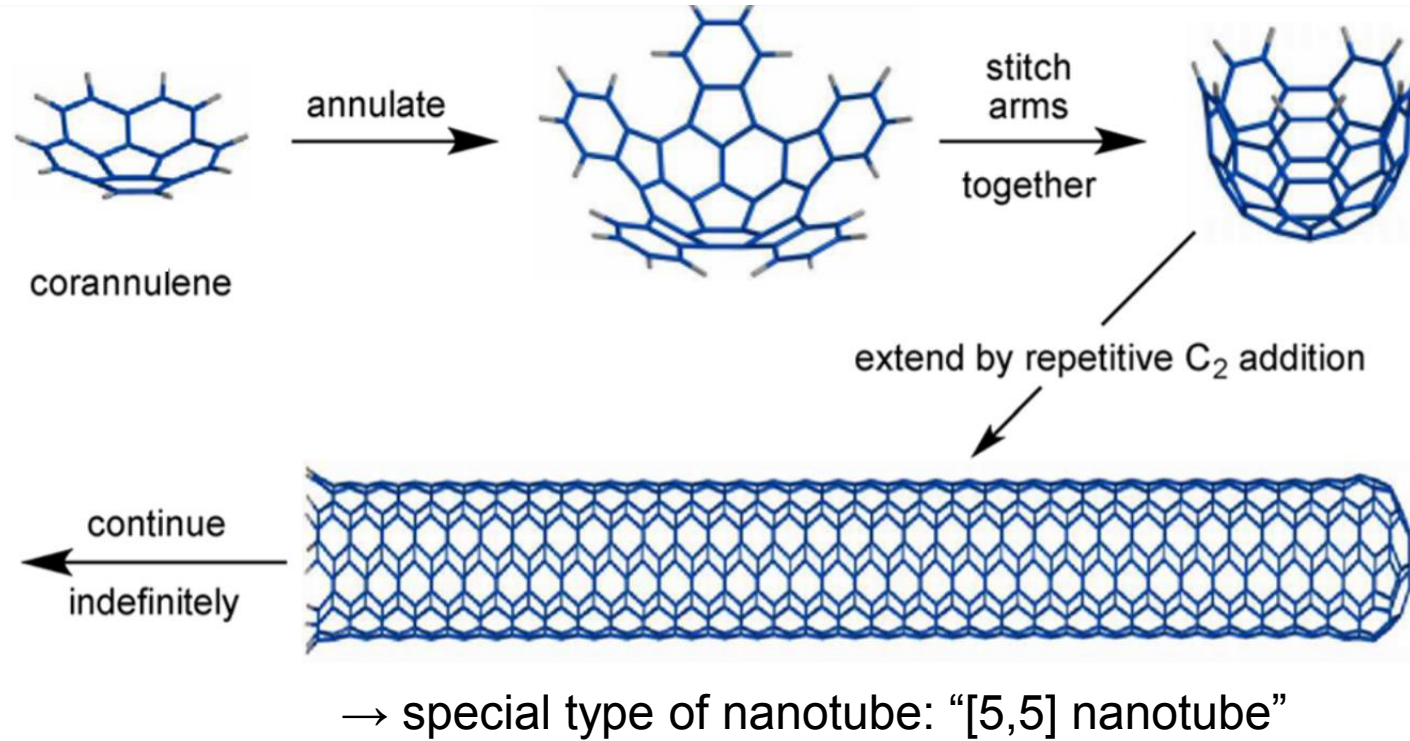
Making the end cap:



(CS_2 is guest, not shown)

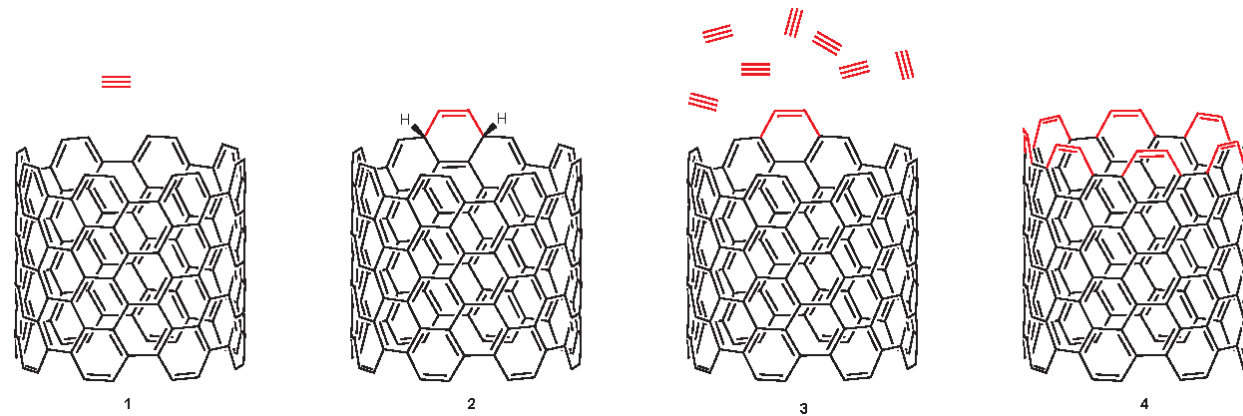
Next: Nanotube synthesis

Nanotube growth strategy: based on corannulene



Next: Nanotube synthesis

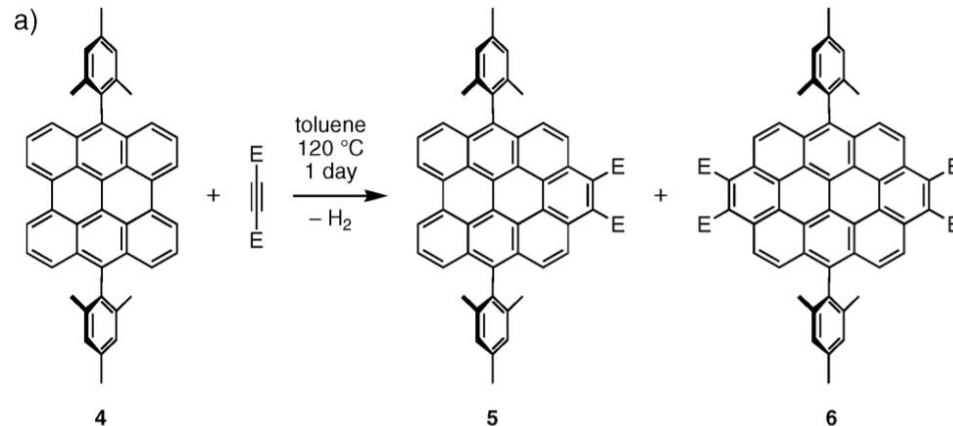
Nanotube growth idea:



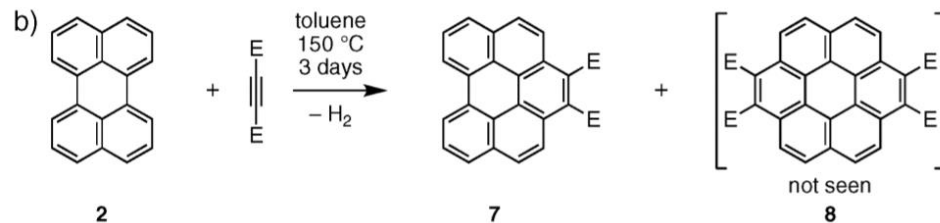
[4 + 2] cycloadditions of ethylene to bay area,
followed by dehydrogenation.
→ there is always a bay area open

Model System:

Cycloaddition to bay with
activated acetylenes (E = $-\text{CO}_2\text{Et}$):



in solution synthesis,
complete conversion



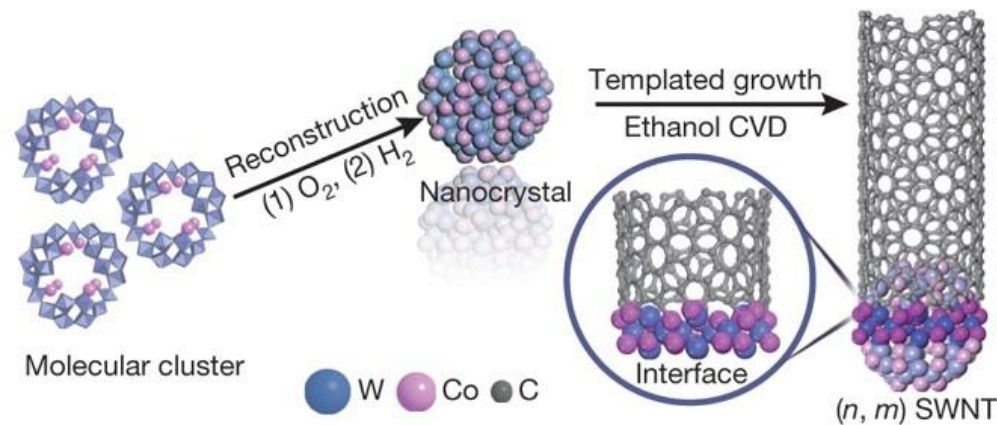
in solution synthesis,
incomplete conversion,
and much slower than “higher annulation” substrates
(see above)

→ the longer the tube fragment, the more efficient the addition.

Finally: Nanotube growth – Brief Introduction to the Topic

- **Typical synthesis of nanotubes (widely used):**
nucleation in “chemical vapor deposition” (CVD) furnace from metal oxide clusters as catalyst (oxide nanoclusters), when carbon-rich gas is inserted (e.g. methane, ethanol, ethylene, acetylene, propene, etc.), see for example:

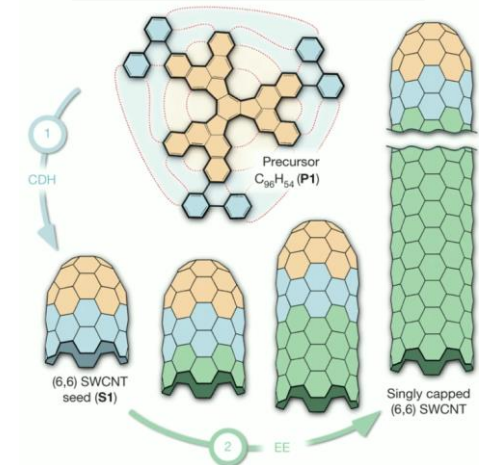
K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima *Science* **2014**, *306*, 1362–1364



Li et al. *Nature* **2014**, *510*, 522–524

- usually mixtures of size & chirality of tubes
- rarely reports on high purity:
pure [6,6] SWCNTs on single-crystal Pt surface by using organic molecules as seeds in UHV:

K. Amsharov, R. Fasel, and co-workers
Nature **2014**, *512*, 61–64



- **NOW Scott** (in collaboration with C. Zhou from Univ. Southern Calif., LA):
Nucleation from his pure corannulene-based “end cap” (no Fe contamination (ICP-MS proven)).

→ **Critical aspects:**

- Any contamination in the grow chamber must be excluded.
- Only pure 5,5 Nanotube is expected to form corannulene endcap nucleation

B. Liu, J. Liu, H.-B. Li., R. Bhola, E. A. Jackson, L. T. Scott, A. Page, S. Irle, K. Morokuma, C. Zhou *Nano Letters* **2015**, *15*, 586–595.

Finally: Nanotube growth – preliminary results

- **Scott's and Zhou's Result:** Obtained nanotubes, but rather unexpected diameter distribution and mixed chirality.

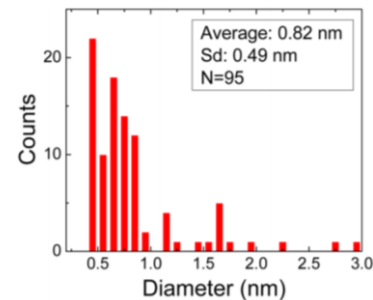
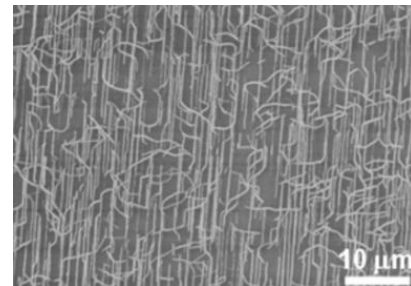
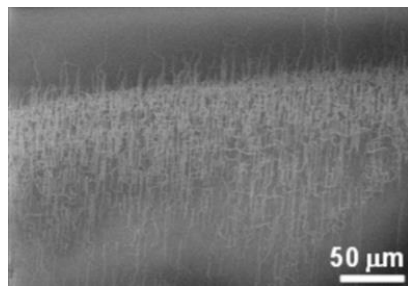
“Nearly Exclusive Growth of Small Diameter Semiconducting Single-Wall Carbon Nanotube from Organic Chemistry Synthetic End-Cap Molecules”

Statement in the Paper:

“...there are no (5,5) SWCNTs grown in the products. The lack of (5,5) SWCNTs is still very puzzling to us at this stage, which needs further study.”

Growth conditions in CVD furnace from the corannulene endcap on quartz surface:

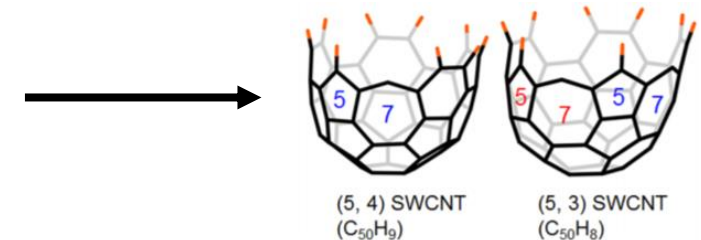
After some pretreatments, mixed $\text{CH}_4/\text{C}_2\text{H}_4$ (= 1300/10 sccm) together with H_2 (300 sccm) were introduced to initiate nanotube growth at 900 °C, typically for 15 min



→ only semiconducting single-walled carbon nanotubes formed (97% purity). This is among the purest growth results so far reported.

Given possible reasons for the mixture of sizes and chiralities:

- 1) Dehydrogenation of endcap forms various “geodesic endcaps” as nucleation point
- 2) aggregation of corannulene endcap to larger clusters nucleates larger tubes



Lawrence T. Scott

„The man who dreams of tubes“

The story might continue:

- 1) academic family tree, e.g.
 - Michel Rickhaus (Zurich)
 - Ihsan Erden (Cal. State, SF)

- 2) Influenced currently active PI's in the field
 - e.g. Ramesh Jasti (Eugene, Oregon)

...and many more...