

Flash vacuum pyrolysis (FVP) or flash vacuum thermolysis (FVT) is a process by which a substrate is distilled through a hot tube and the products are collected afterwards in a cold trap.

–Unimolecular conditions
–High temperatures (200–1000 °C), but short exposure times (~ms)
Therefore, there are only a few parameters to optimize, namely temperature, time of exposure (related to initial heating, pressure, and carrier gas), and occasionally solid-phase packing material.

Reactions typically fall into the following categories:

–Pericyclic processes (entropy often favors "reverse" direction)
–Cleavage of small molecules (N₂, CO₂, CO, ethylene, etc.)
–Cleavage of the weakest bond in the molecule to afford free radicals

Since these processes are dominated by cleavage mechanisms, FVP reactions are *oxidative* rather than reductive.

Ionic mechanisms are never encountered under FVP due to high ionization energies in the absence of solvation.

"FVP should not be considered a molecular sledgehammer, even if apparently extreme temperatures are employed."

Glassware for Flash-Vacuum Thermolysis

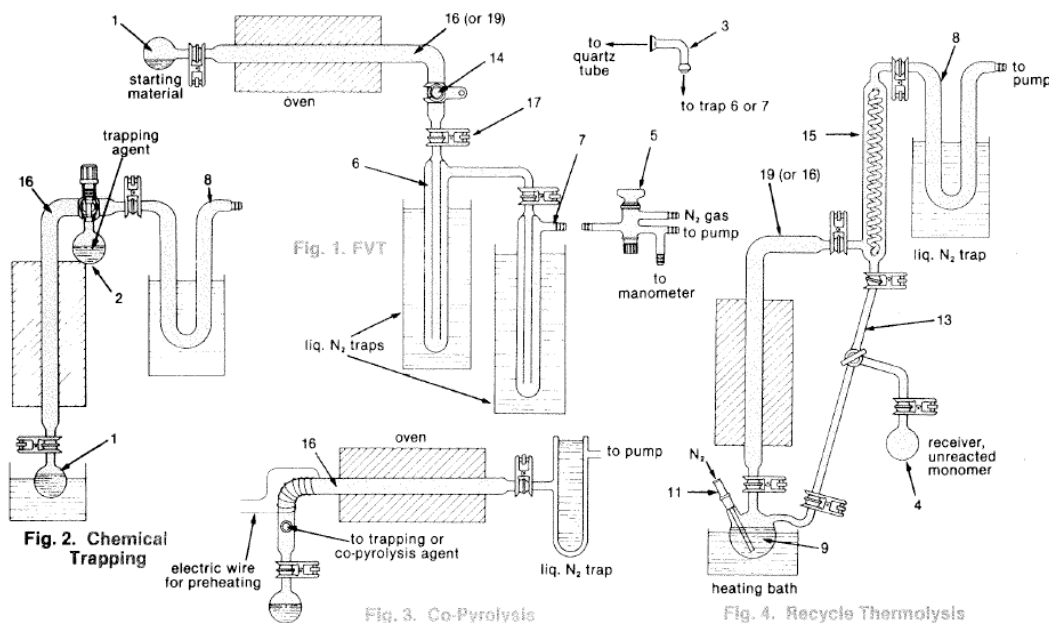
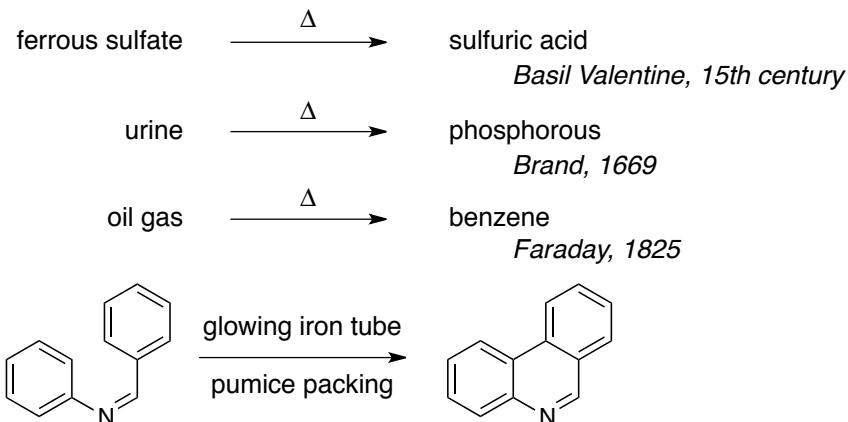


Fig. 3. Co-Pyrolysis
Aldrichimica Acta 1984, 17, 31.

"The destructive distillation of mineral or organic material was one of the few preparative methods available to the alchemists and the first chemists."



Ber. Dtsch. Chem. Ges. 1899, 22, 3339.
Justus Liebigs Ann. Chem. 1891, 1, 49.

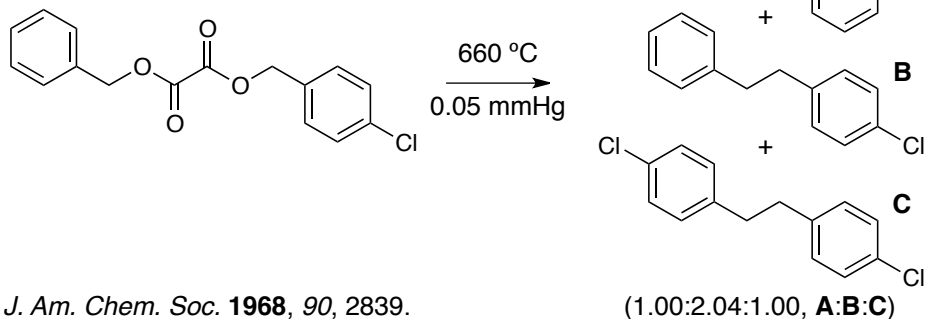
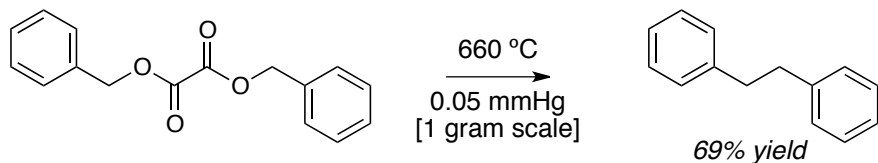
Cost of FVP apparatus?

- Standard laboratory vacuum
- Quartz tubing (<\$100, www.technicalglass.com)
- Tube furnace (\$2500.00+, www.coleparmer.com)
- Typical glassware

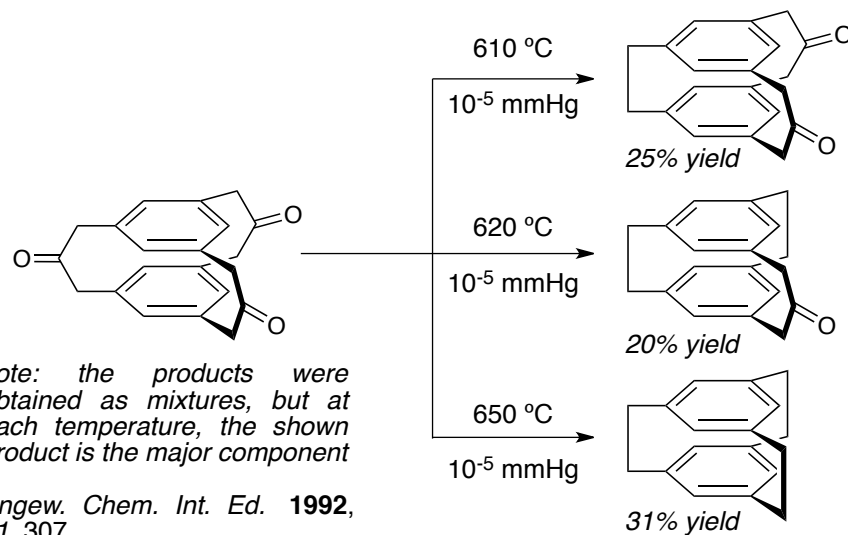
Notable Reviews:

- Angew. Chem. Int. Ed. Engl.* 1977, 16, 365.
- Brown, R.F.C. *Pyrolytic Methods in Organic Chemistry*, Academic Press, 1980.
- Tetrahedron*, 1986, 42, 2135.
- Thermochemica Acta* 1987, 112, 31.
- Pure & Appl. Chem.* 1990, 62, 1981.
- Contemp. Org. Syn.* 1996, 3, 373.
- Eur. J. Org. Chem.* 2001, 2209.
- Aldrichimica Acta* 2004, 37, 19.
- "Pyrolysis, Flash Vacuum," in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2006; pp 134–158.
- Aust. J. Chem.* 2010, 63, 1002.

Alkane formation

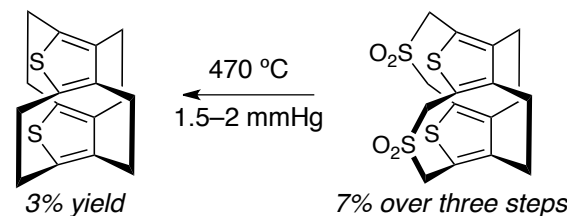
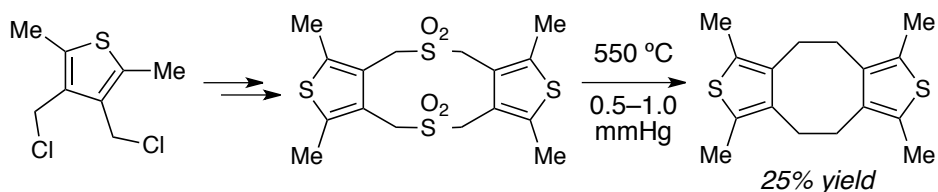
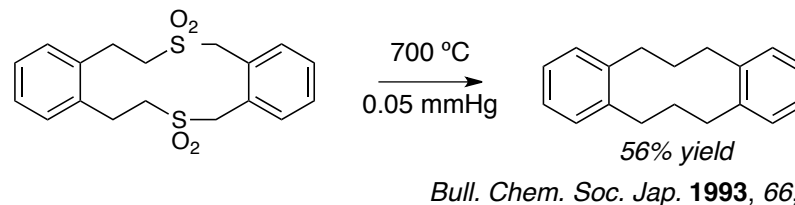


J. Am. Chem. Soc. **1968**, *90*, 2839.



note: the products were obtained as mixtures, but at each temperature, the shown product is the major component

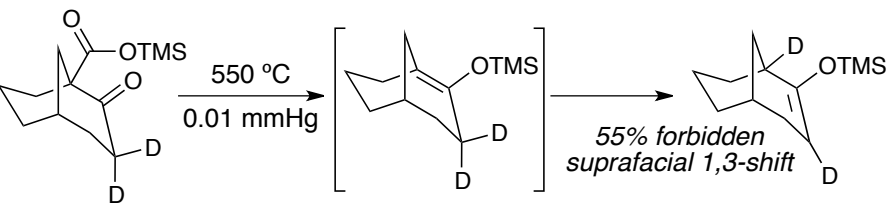
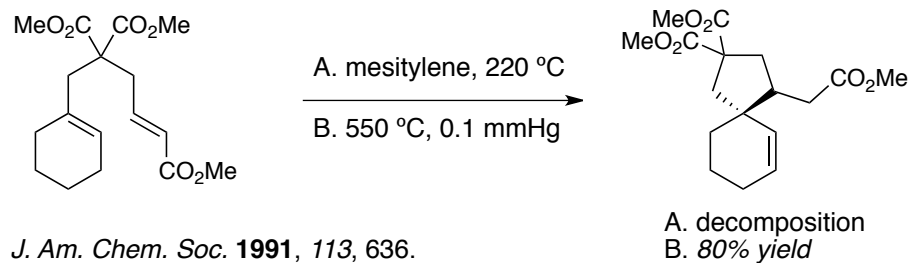
Angew. Chem. Int. Ed. **1992**, *31*, 307.



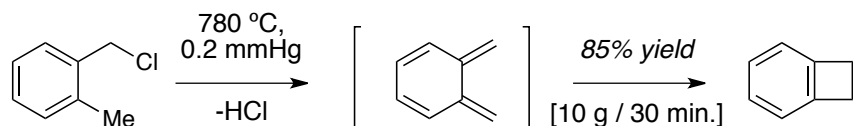
1. NBS
2. Na₂S·9H₂O
3. mCPBA

J. Org. Chem. **1992**, *57*, 4654.

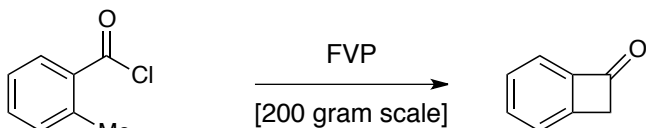
Alkene formation



J. Chem. Soc. Perkin Trans. 1 **1976**, 371. + 3% retro DA, 37% enol hydrolysis

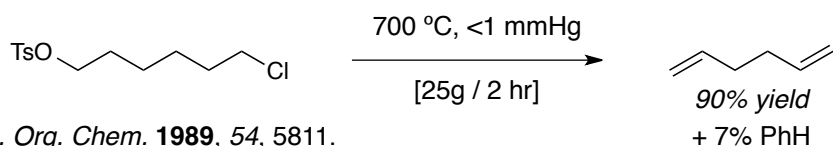
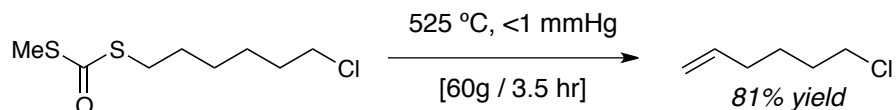
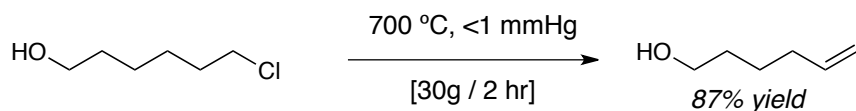


Synthesis, 1992, 1265.

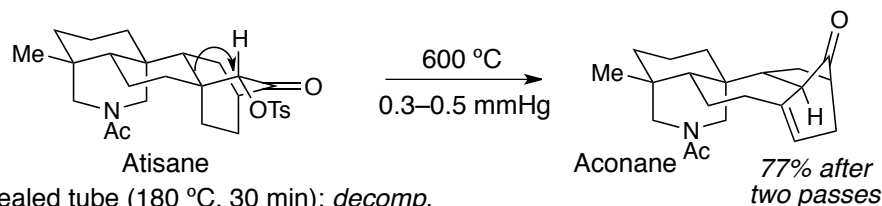


Run	1	2	3	4	5	6	7	8
Column Temp. (°C)	630	630	780	780	780	800	800	780
Pressure (mmHg)	14	5	5	5	1.75	1.75	1.5	0.5
Yield (%)	28	53	59	60	35	32	75	80

Tetrahedron Lett. 1998, 39, 1695.



J. Org. Chem. 1989, 54, 5811.

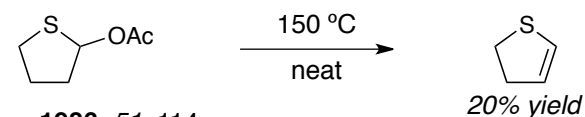
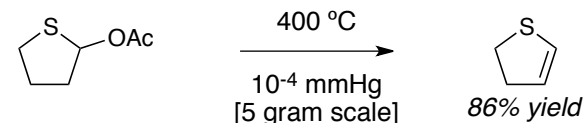


Sealed tube (180 °C, 30 min): *decomp.*

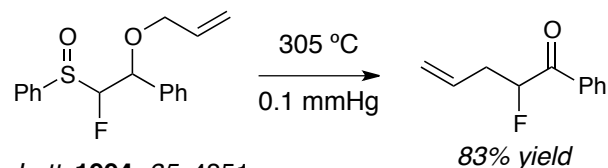
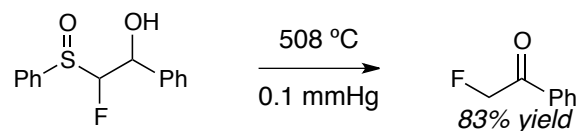
Reflux in collidine (180 °C, 18h): *n.r.*

Sublimation (300 °C, 0.1 mmHg): *low conversion*

J. Chem. Soc., Perkin Trans. 1 1972, 1490.

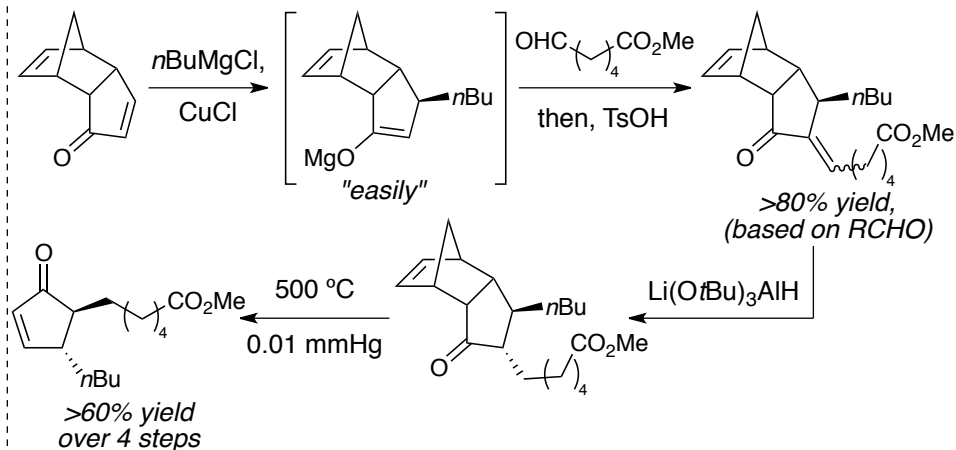


J. Org. Chem. 1986, 51, 114.



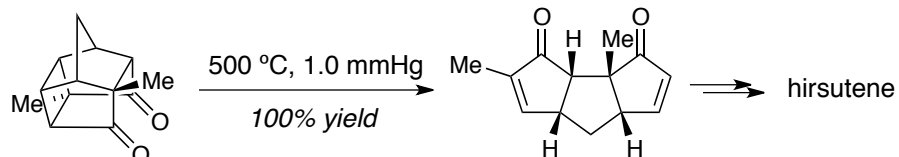
Tetrahedron Lett. 1994, 35, 4851.
Tetrahedron Lett. 1994, 35, 4853.

An approach toward the prostainoids



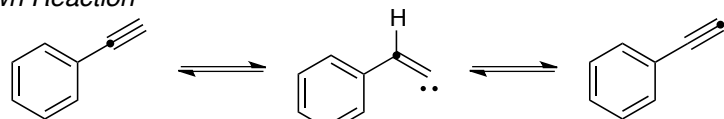
J. Chem. Soc., Chem. Commun. 1976, 12, 446.

For more on the concept of "transient chirality" utilizing retro-DA methodology, see: Chem. Rev. 1999, 99, 1163.

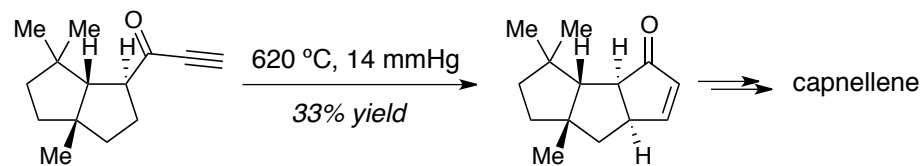


Tetrahedron, **1981**, 37, 4543.
See also: Weidner, Triquinane GM, 2012.

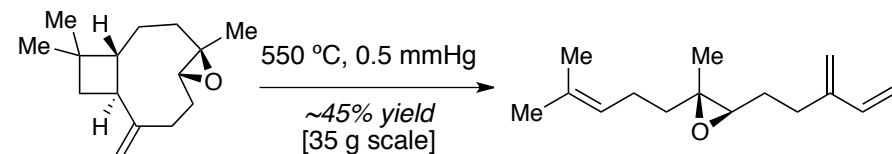
The Brown Reaction



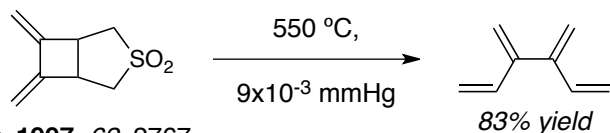
J. Chem. Soc., Chem. Commun. **1973**, 123.



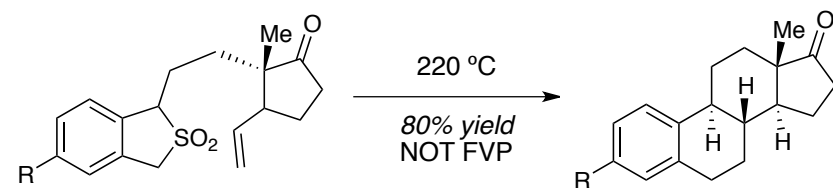
Helv. Chim. Acta **1982**, 65, 2413.



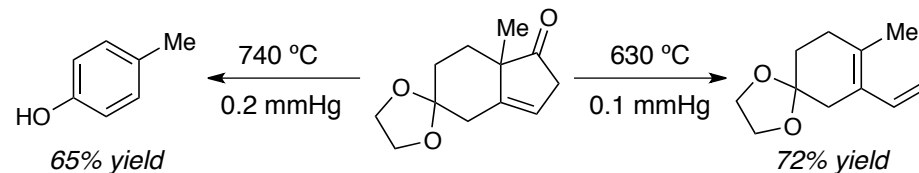
Helv. Chim. Acta **1994**, 77, 36.



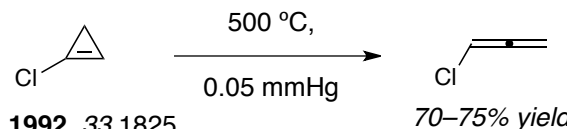
J. Org. Chem. **1997**, 62, 2767.



Helv. Chim. Acta **1980**, 63, 1703.

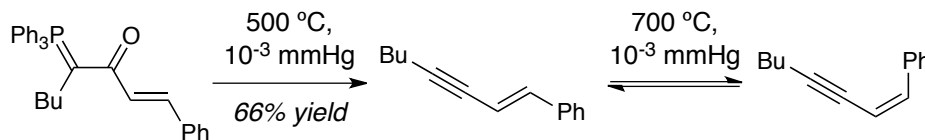
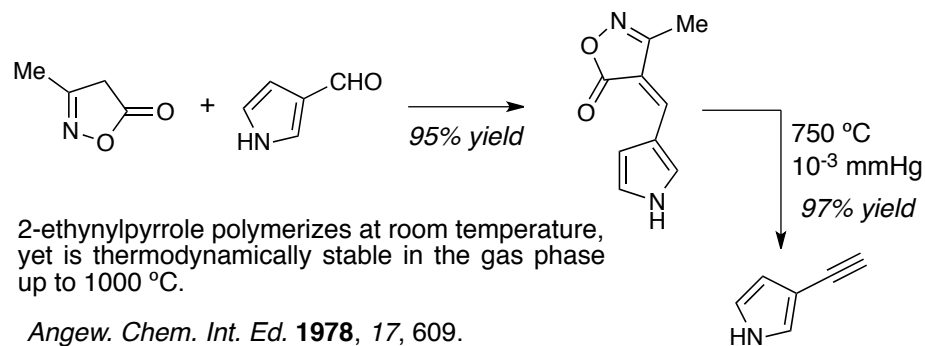
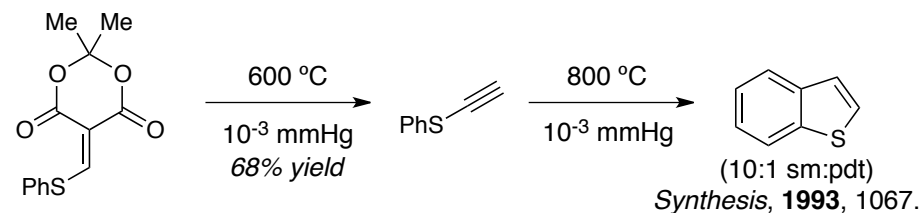


Aust. J. Chem. **1984**, 37, 2295.



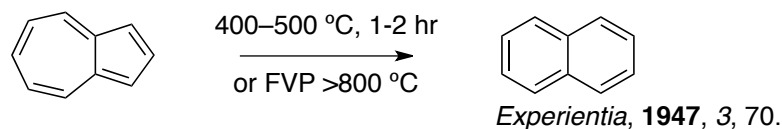
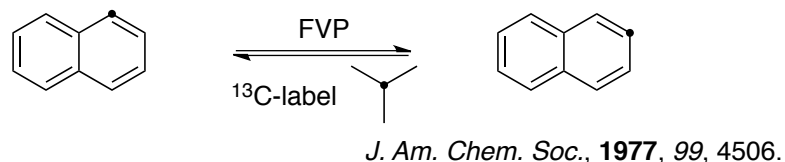
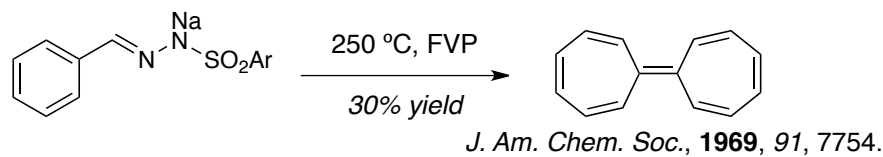
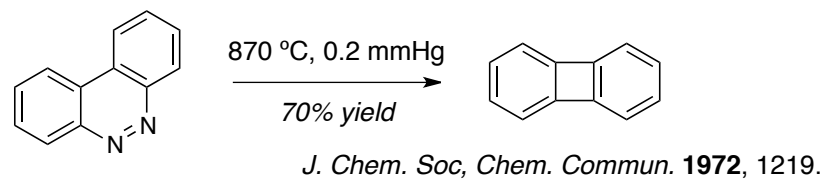
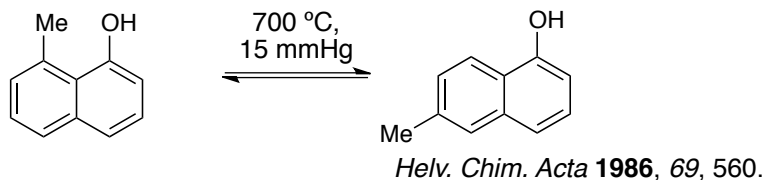
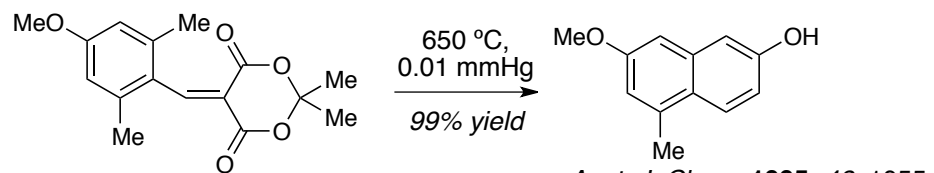
Tetrahedron Lett. **1992**, 33, 1825.

Alkyne formation



J. Chem. Soc., Perkin Trans. 1, **1994**, 2473.

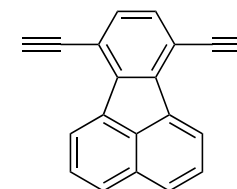
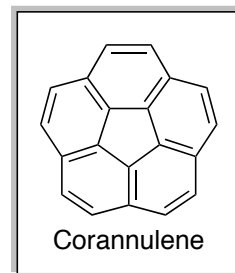
Aromatic Chemistry



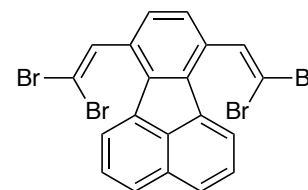
Extensive ¹³C-labelling studies and DFT calculations show that multiple mechanisms are operative, which are interesting, complex, and out of the scope of this group meeting. For a thorough discussion, see:

Acc. Chem. Res. **1982**, 15, 52.

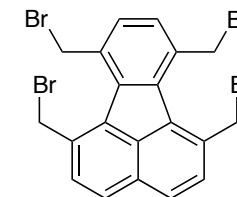
J. Am. Chem. Soc. **2003**, 125, 5375.



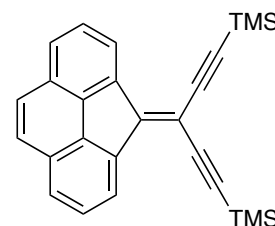
1000 °C, 10⁻⁴ mmHg
10% yield, 30–50 mg scale
J. Am. Chem. Soc. **1991**, 113, 7082.



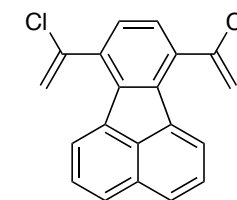
900 °C, 10⁻⁴ mmHg
23% yield, 50 mg scale
J. Am. Chem. Soc. **1992**, 114, 1920.



1000 °C, FVP
18% yield, 60 mg scale
J. Am. Chem. Soc. **1992**, 114, 1921.



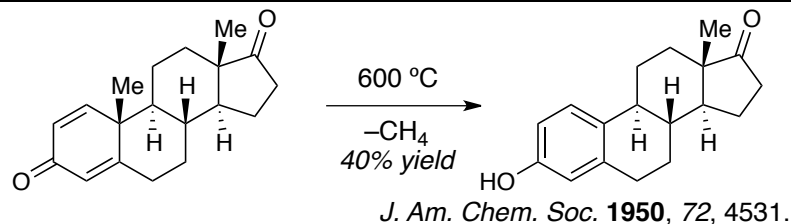
900 °C, FVP, H₂ carrier gas
15% yield, 20–40 mg scale
Tetrahedron Lett. **1994**, 35, 4747.



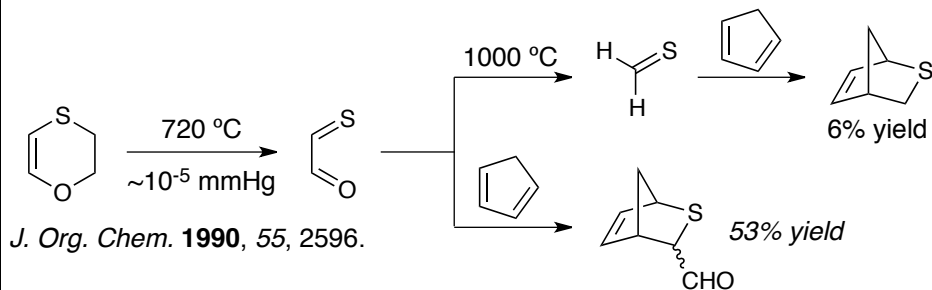
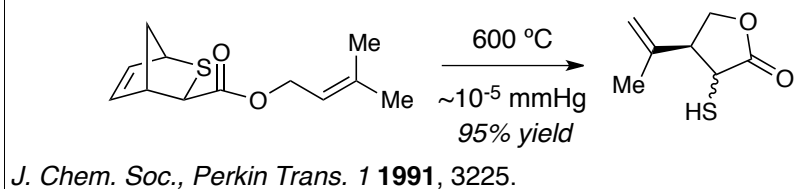
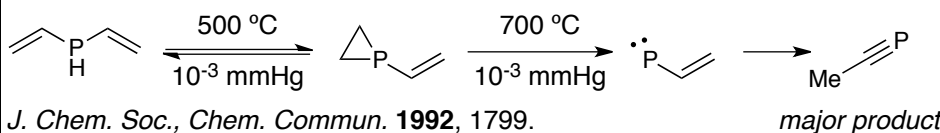
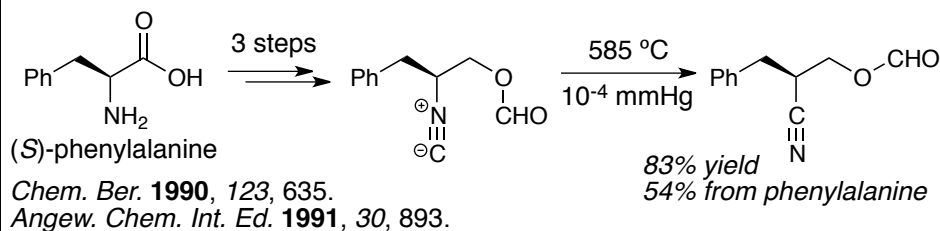
1100 °C, 1.0 mmHg
N₂ carrier gas, 1.0 g scale, 40% yield
J. Am. Chem. Soc. **1997**, 119, 10963.

For a higher-yielding, solution-phase approach based on similar disconnections, see: *J. Am. Chem. Soc.* **2000**, 122, 6323.

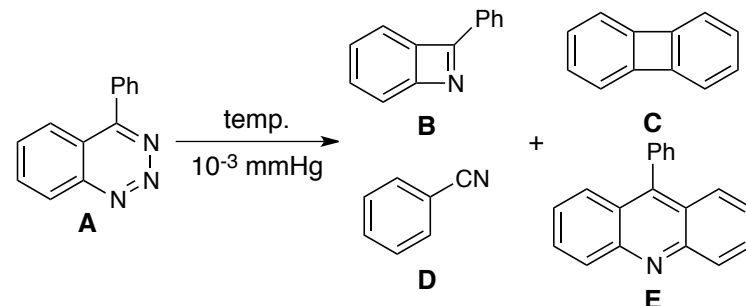
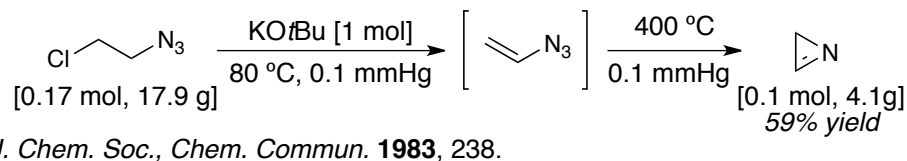
For additional synthesis of and studies on *geodesic polyarenes*, see: *Chem Rev.* **2006**, 106, 4868.



Heteroatom Containing Functional Groups



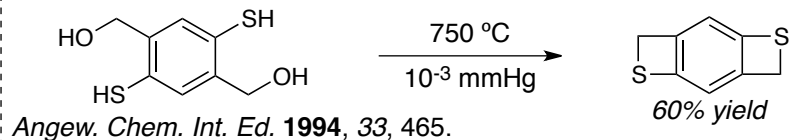
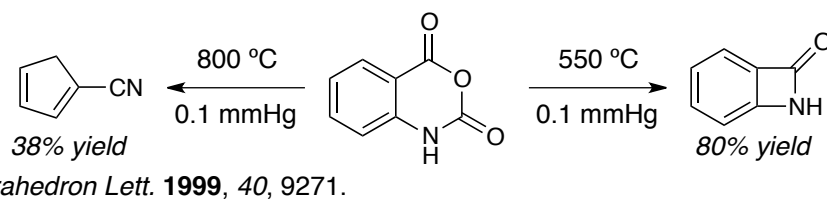
Heterocyclic Chemistry

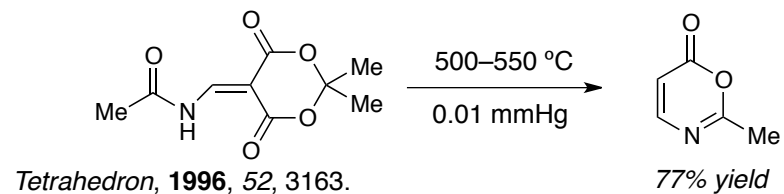
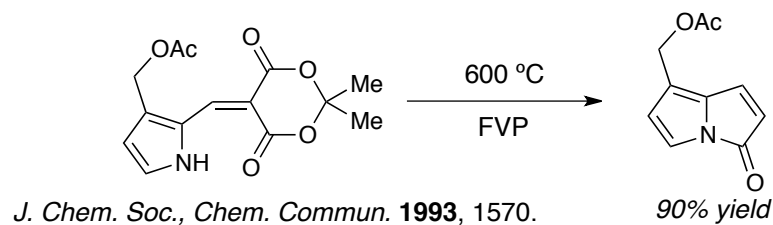
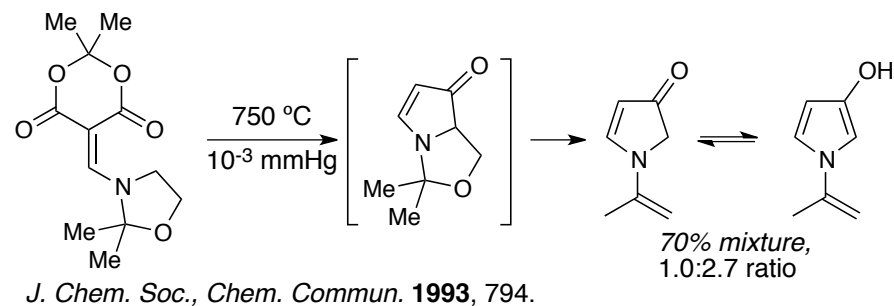
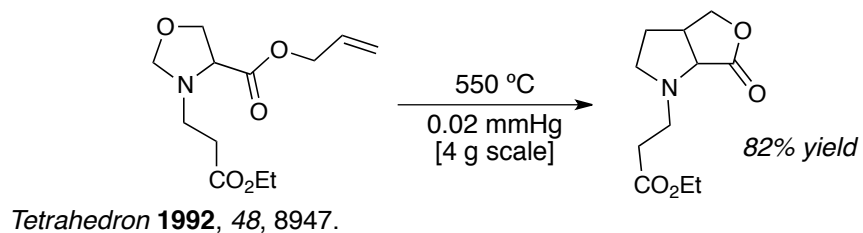
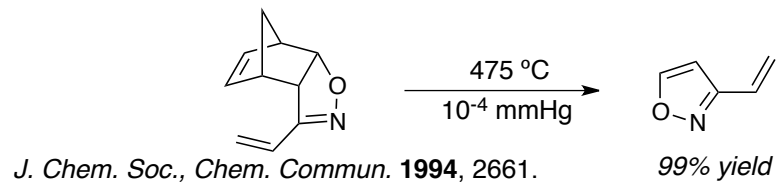
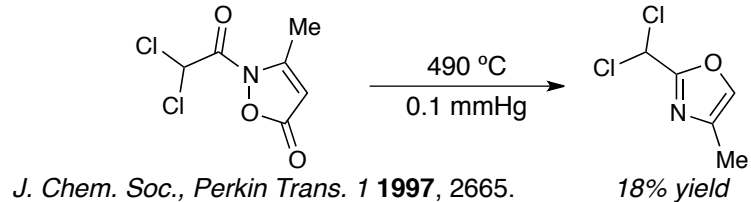
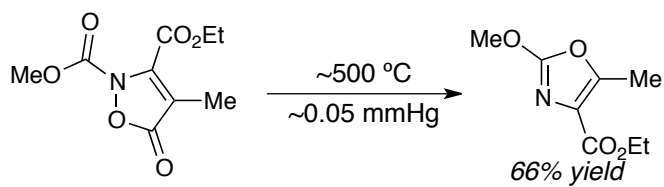
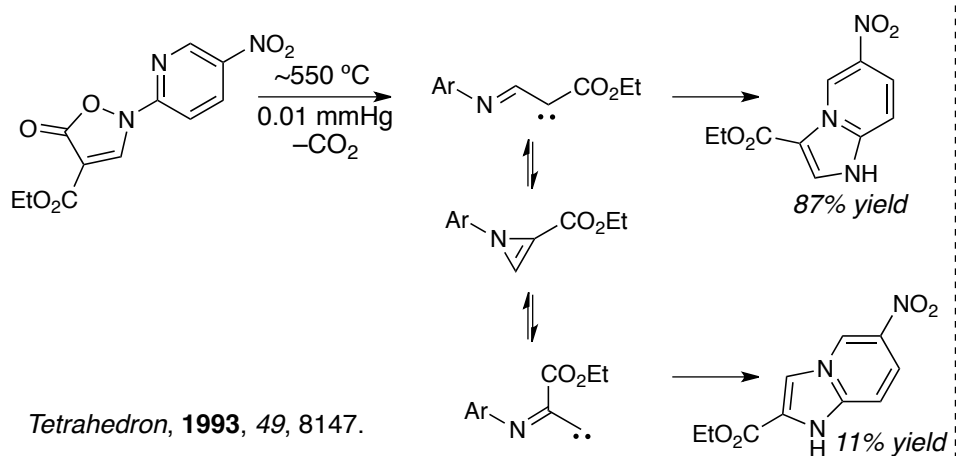
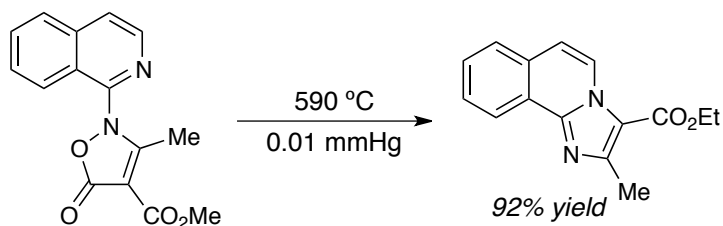


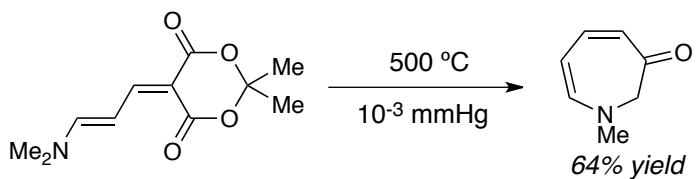
temp. (°C)	A	B	C	D	E
400	100%	-	-	-	-
420-450	some	>64%	some	some	some
>500	-	-	some	some	-

(+ charred material)

J. Chem. Soc., Perkin Trans. 1, **1975**, 45.



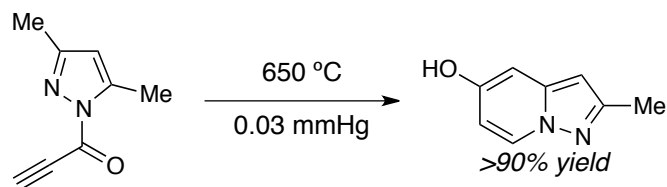




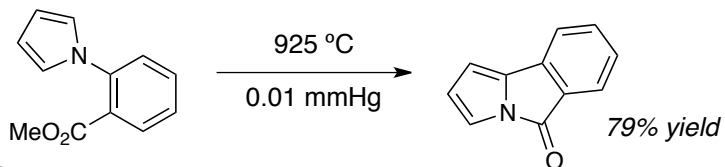
J. Chem. Soc., Chem. Commun. **1987**, 140.

J. Chem. Soc., Perkin Trans. 1 **1989**, 425.

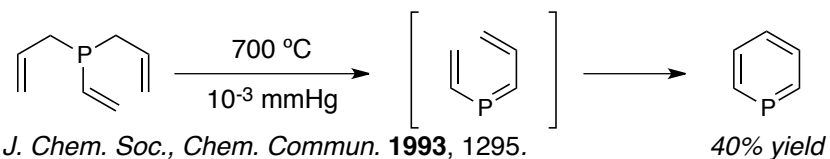
For a review containing an overview of FVP with Meldrum's acid derivatives, see: *Aldrichimica Acta* **2004**, 37, 19.



Aust. J. Chem. **1994**, 47, 991.



J. Chem. Soc., Perkin Trans. 1 **1999**, 2047.



J. Chem. Soc., Chem. Commun. **1993**, 1295.

