

The elements:

**Tellurium:** Discovered in 1782 as a gold telluride mineral. Named from *tellus*, the Latin word for "earth." The percent of relative elemental abundance for the universe is far higher than that on Earth, partly because Te forms  $\text{TeH}_2$ , which is volatile so it escapes the Earth. Te has no biological function, but some fungi can incorporate it into peptides in the place of S or Se.

**Thallium:** Discovered in 1861. It produced a green spectral line by flame spectroscopy, so it is named after *thallos*, the Greek word for "a green shoot or twig." It is usually at the +1 or +3 oxidation state.  $\text{Tl}^+$  ions are similar to  $\text{Ag}^+$  and  $\text{K}^+$  in size, and *in vivo* they are pumped into cells through potassium channels, and once inside the cell thallium binds to sulfur in cysteine residues and ferredoxins.  $\text{Tl}^{3+}$  ions resemble softer versions of boron and aluminum Lewis acids, and are also a potent oxidants.

**Lead:** Discovered roughly 9000 years ago in the middle east. In atomic physics,  $^{208}\text{Pb}$  is "double magic" because it has 82 protons and 126 neutrons, making it exceptionally stable to radioactive decay. In animals, lead accumulates in the tissues and bones, as well as attacks the nervous system.

Why are they not used?

**Tellurium:** Not very toxic, but relatively rare and expensive. Humans exposed to as little as  $0.01 \text{ mg/m}^3$  or less of Te metal in air exude a foul garlic-like odor known as 'tellurium breath'" (Wikipedia: "Tellurium"). Most organisms metabolize tellurium to dimethyl telluride, the source of the smell. Other organo tellurides do not smell bad. Mostly perception is why it's not used.

**Thallium:** Crazy toxic. "Poisoner's poison":  $\text{Tl(I)}$  salts are tasteless and odor-free. Also, symptoms of thallium poisoning are similar to other illnesses, so physicians are often confused. Unlike mercury and lead, however, thallium is not a bioaccumulative poison.

**Lead:** Toxic, but not as toxic as public perception leads you to believe. By weight, palladium is more toxic than lead, and some authors in the literature claim palladium is ten times more toxic. Lead is abundant and has many industrial applications, so you're more likely to be affected by it. Pb tends to have high ligand coordination numbers (4-7, even as high as 8 or 9), so making as using well-defined organoplumbanes can be difficult.

**Relative abundance in the earth's crust**

**Oral LD50 for rat** (Sigma Aldrich's MSDS's)  
 $\text{Pb(OAc)}_2$ : 4665 mg/kg  
 $\text{Pd(OAc)}_2$ : 2100 mg/kg  
 $\text{TlCl}$ : 24 mg/kg  
 $\text{TeO}_2$ : > 5000 mg/kg Note: Diarrhea  
 $\text{SeO}_2$ : 68.1 mg/kg

Element	ppm
<b>Lead</b>	<b>14</b>
Tin	2.2
<b>Thallium</b>	<b>0.6</b>
Iodine	0.14
<b>Tellurium</b>	<b>0.005</b>
Platinum	0.003
Gold	0.0011

					helium 2 He 4.0026	
	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
unubium 112 Uub [277]		ununquadium 114 Uuq [289]				



Tellurium



Thallium



Lead

**Main Sources:**

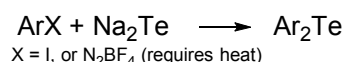
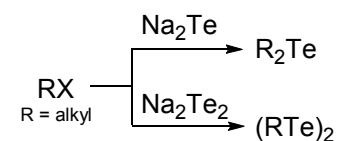
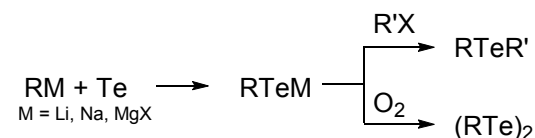
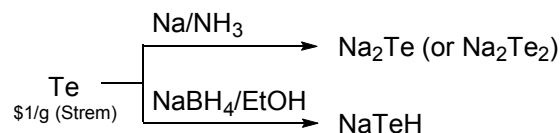
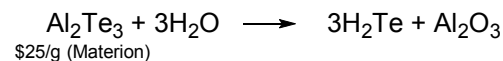
"Main Group Metals in Organic Synthesis", 2004, edited by H. Yamamoto and K. Oshima. Chapters 9, 13, and 15.

**Reviews:**

**Te:** Synthesis 1991, 793 & 897. Tetrahedron 2005, 1613. Chem. Rev. 2006, 1032.  
**Tl:** Synthesis 2010, 1059. Synthesis 1999, 2001. Acc. Chem. Res. 1970, 338.  
**Pb:** Tetrahedron 2001, 5683.

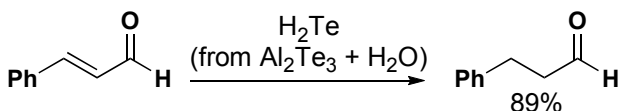
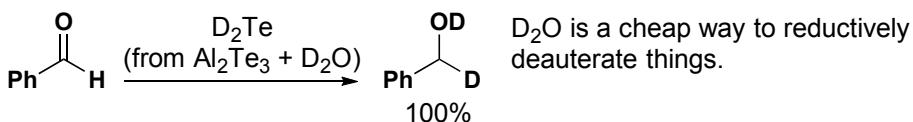
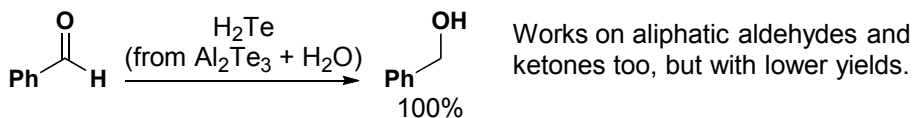
## Tellurium reagents and making C-Te bonds

See book chapter



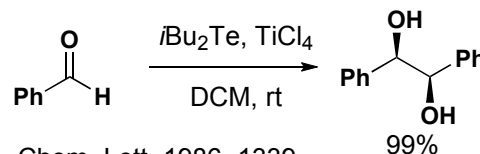
## Reduction

ACIE 1980, 1009



Other reductions possible with Te reagents (such as NaTeH, PhTeSiMe<sub>3</sub>): aryl alkenes, enamines and imines, nitrones, thio carbonyls, nitro groups, N-oxides, azides. See the reviews, especially Synthesis 1991, 793.

Homogeneous production of Ti(III) species in inert solvents

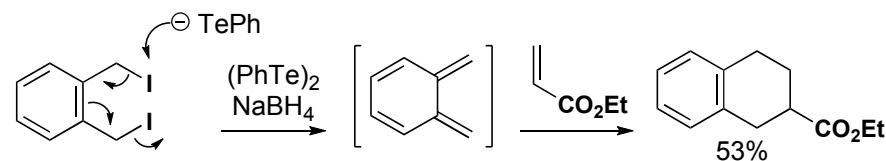


Chem. Lett. 1986, 1339

Only diastereomer. With aqueous TiCl<sub>3</sub> they get a mixture of this and the *meso* isomer.

Dehalogenation

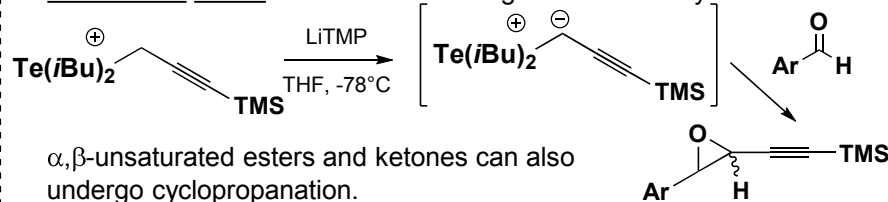
Bull. Chem. Soc. Jpn. 1986, 3013



Other reactions with similar mechanisms: Reformatsky-type, epoxides with an α-LG give allylic alcohols, dealkylation of quaternary ammonium salts, removal of nitro groups, removal of sulfones, and more. See the above review.

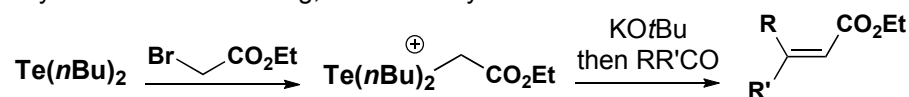
JOC 1992, 6598

Telluronium Ylides ... do the same things as sulfonium ylides



Tet. Lett. 1983, 2599

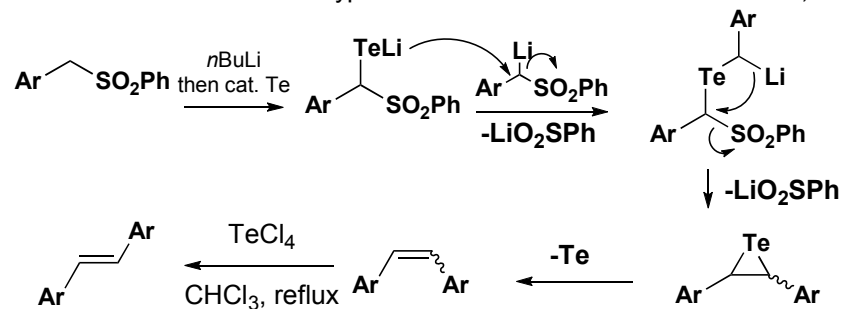
If your HWE isn't working, telluronium ylides can do that too.



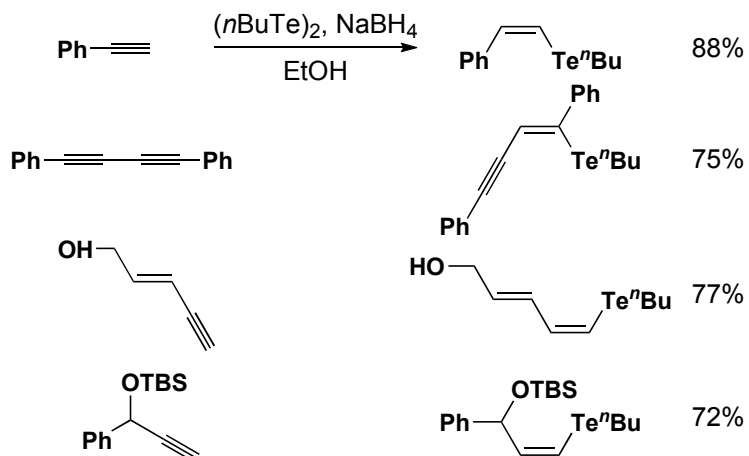
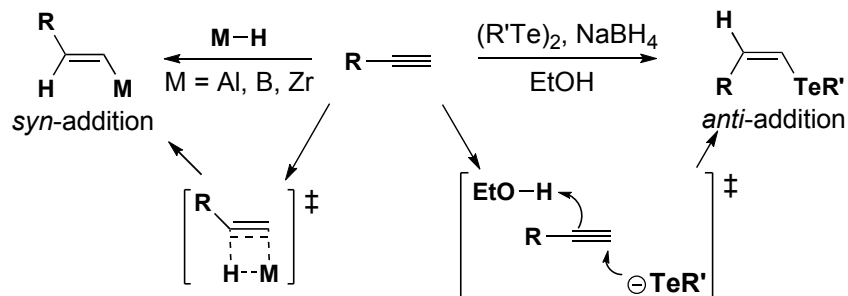
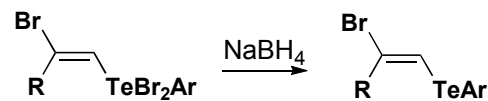
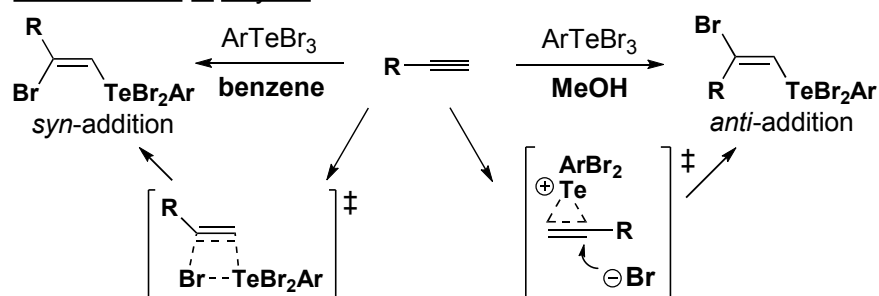
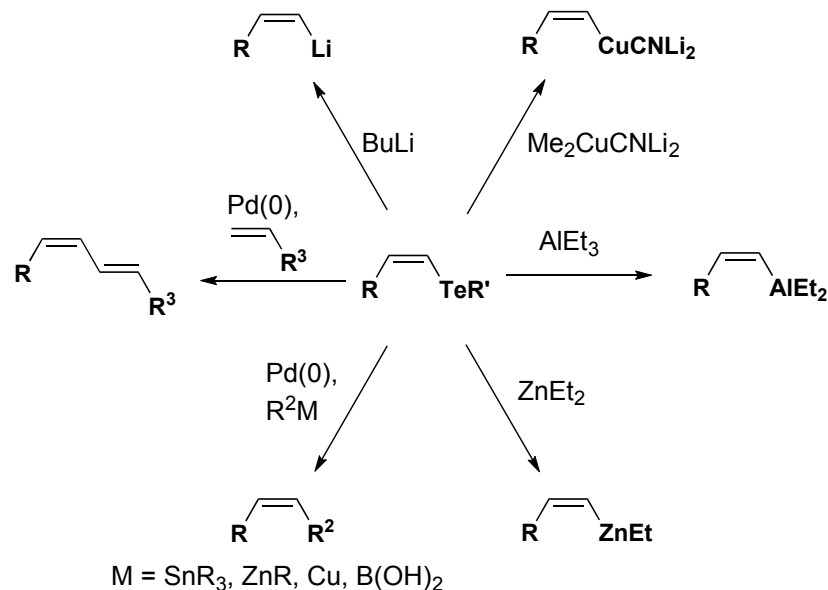
Note: stabilized sulfonium ylides such as these are inert to carbonyl groups.

Or even a Julia-olefination-type dimerization

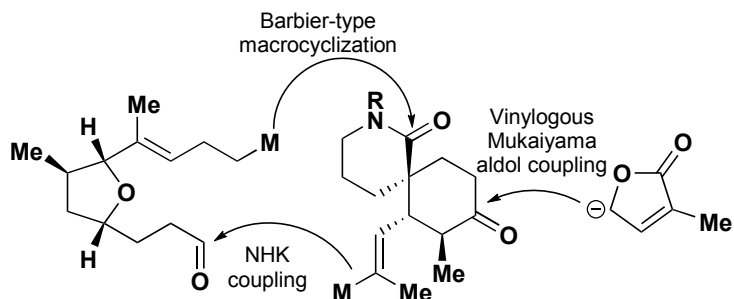
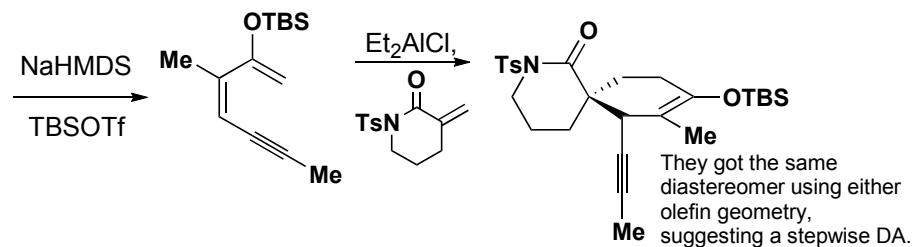
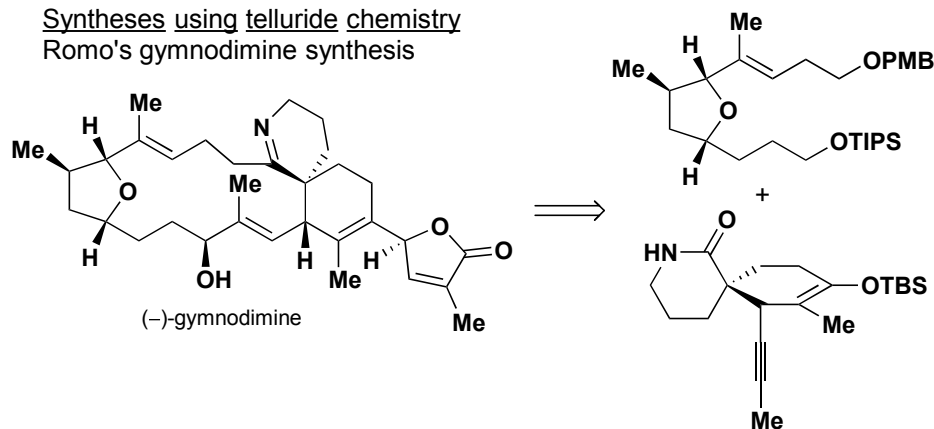
JOC 1984, 3559

Hydrotelluration of alkynes

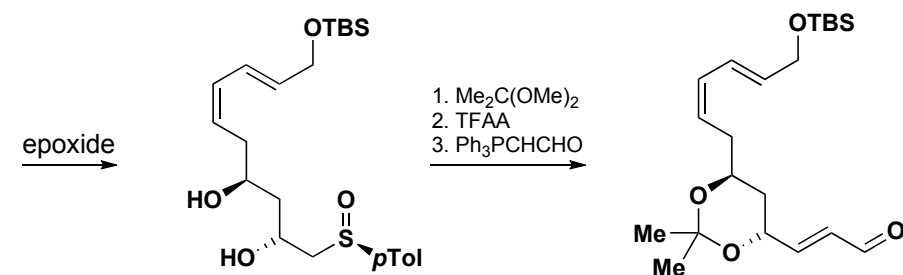
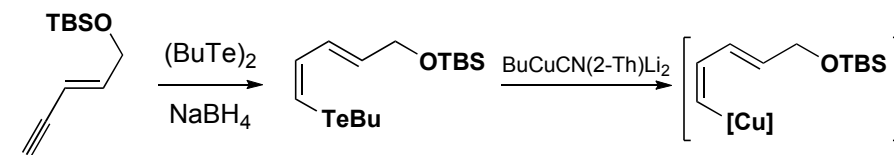
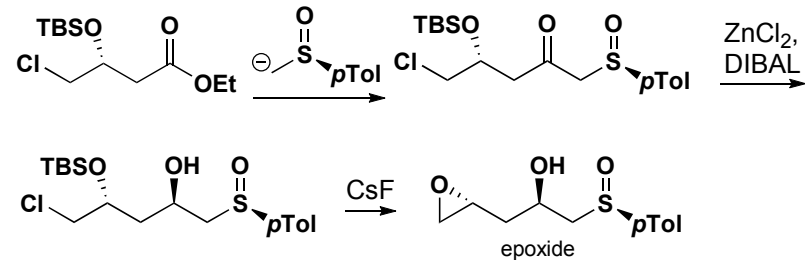
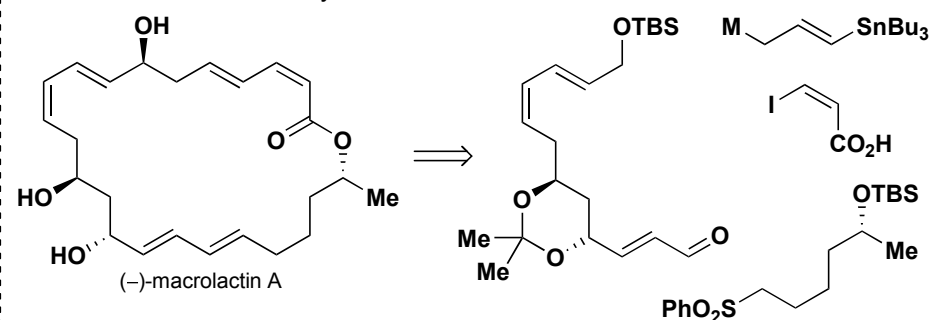
see Chem. Rev. 2006, 1032

Halotelluration of alkynesSo what do you do with all these fancy tellurides you can make?  
Metal-tellurium exchange and direct cross-coupling!

This method also works great for Michael-addition on alkynes bearing an EWG. You can even trap with an electrophile stereospecifically, opening possibilities for stereodefined tetrasubstituted olefins.

Syntheses using telluride chemistry  
Romo's gymnodimine synthesis

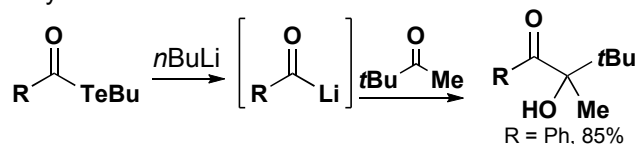
## Marino's macrolactin A synthesis. JACS 2002, 1664



Miscellaneous telluride applications from Li-Te exchange

Acyl anions

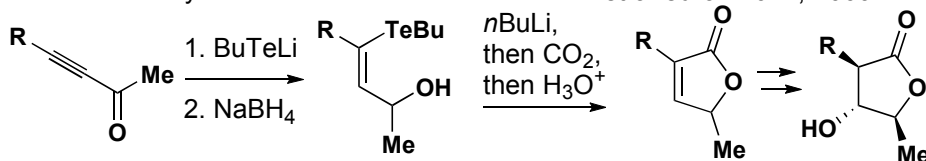
JACS 1990, 455



Acyl stannanes or selenoesters don't do this.

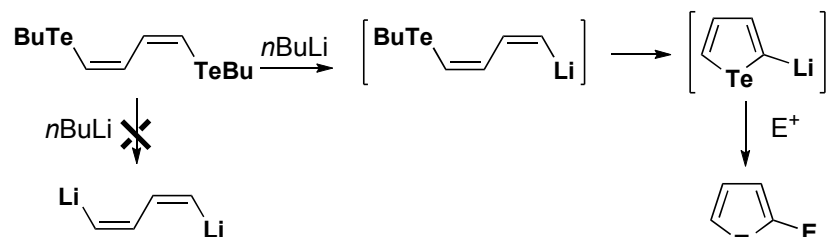
Butenolide synthesis

Tetrahedron 2012, 10601

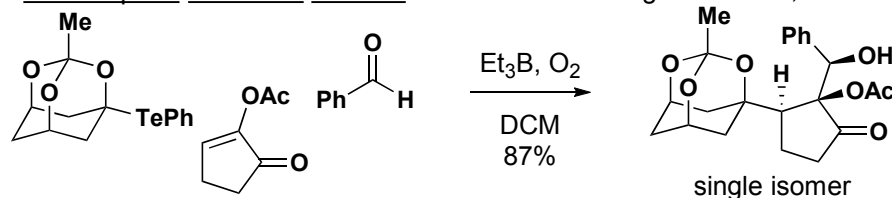


Tellurophene synthesis

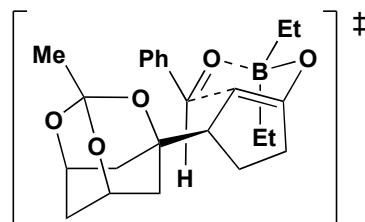
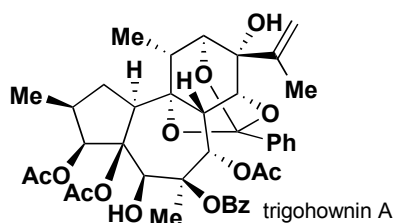
Tetrahedron 1997, 4199

Radical-polar crossover reaction

Org. Lett. 2013, 5122



No reaction with the selenium acetal.

Not covered

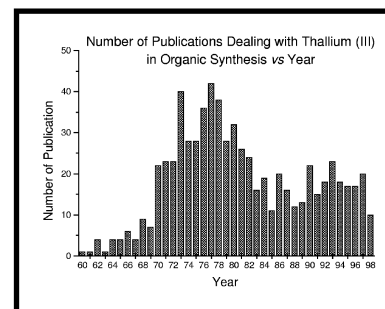
Many more ways to make C-Te bonds!

Allylic oxidations

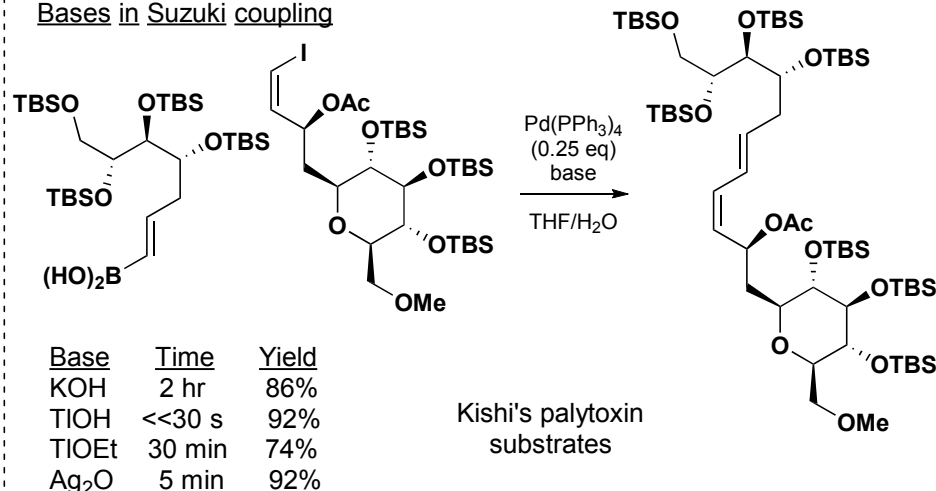
Telluroxide eliminations

Tellurolactonization

Not much on tellurium heterocycles

Thallium

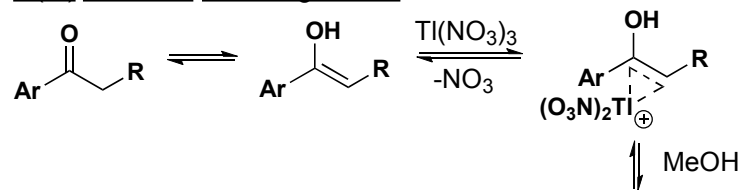
Synthesis 1999, 2001

Standard electrode potentials**Hg(II) → Hg(0) = +0.91 V****Pd(II) → Pd(0) = +0.915 V****Tl(III) → Tl(I) = +1.25 V****Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> → 2Cr(III) = +1.33 V****Pb(IV) → Pb(II) = +1.69 V****MnO<sub>4</sub><sup>-</sup> → Mn(II) = +1.70 V**Bases in Suzuki coupling

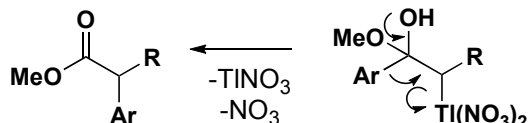
JACS 1987, 4756. See also Org. Lett. 2000, 2691.

These Tl(I) salts also seems to be very capable of alkylating and acylating 1,3-dicarbonyls and phenols. See Acc. Chem. Res. 1970, 338.

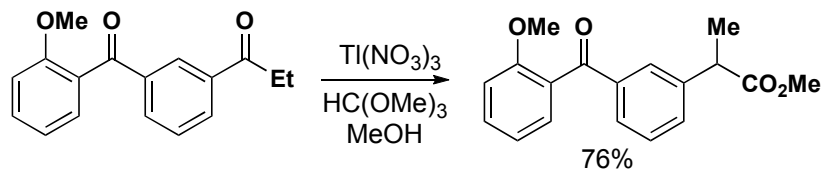
## Ti(III) Oxidative Rearrangements



$\alpha$ -[O] of ketones is also possible by this mechanism, but I won't show any examples.

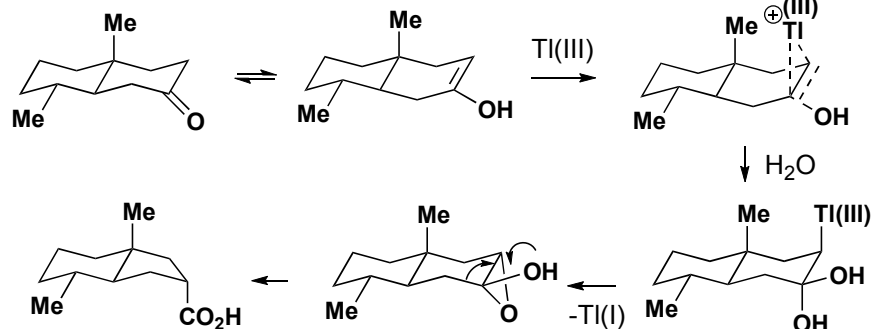
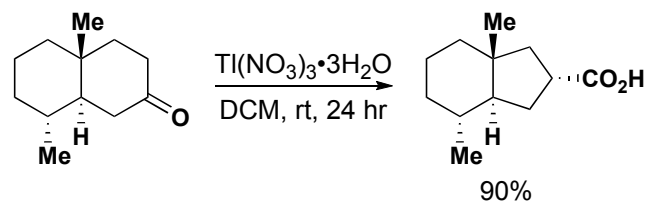
 $\alpha$ -aryl esters from aryl ketones

Synth. Commun. 1995, 3931



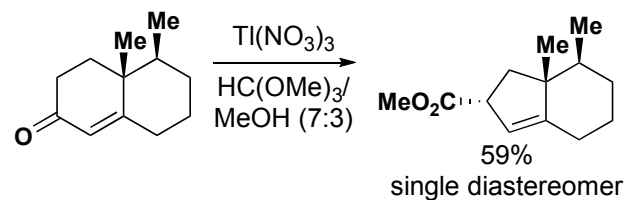
## Ring contraction

JOC 1998, 1716

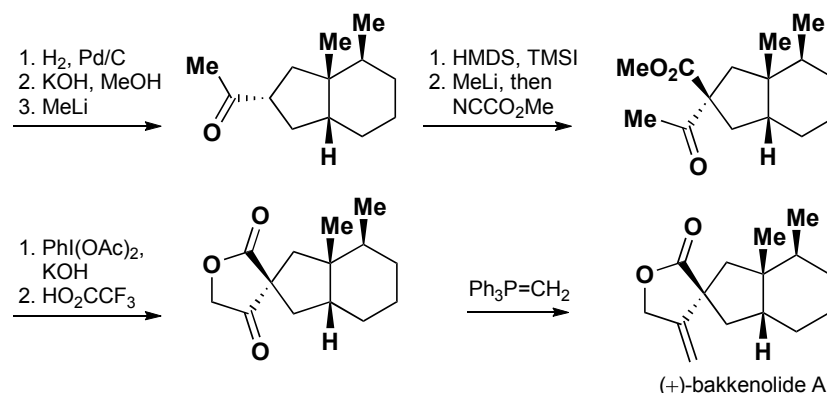


## An example in synthesis of (+)-bakkenolide A

JOC 2010, 2877

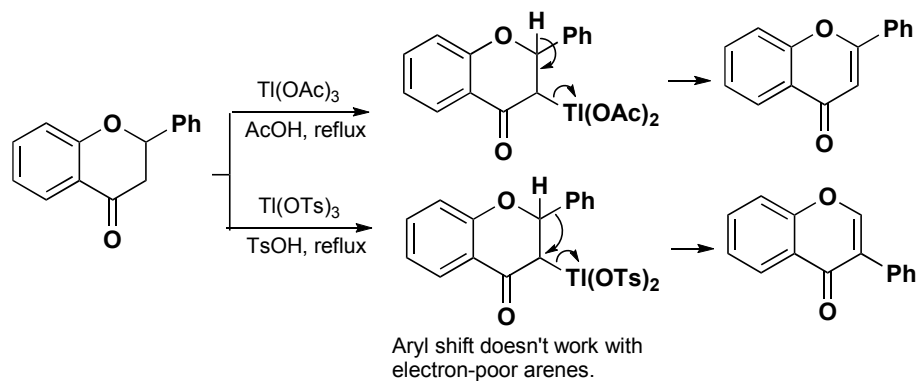


Iodine(III) reagents gave a 1:1 mixture of diastereomers and 40% overall yield



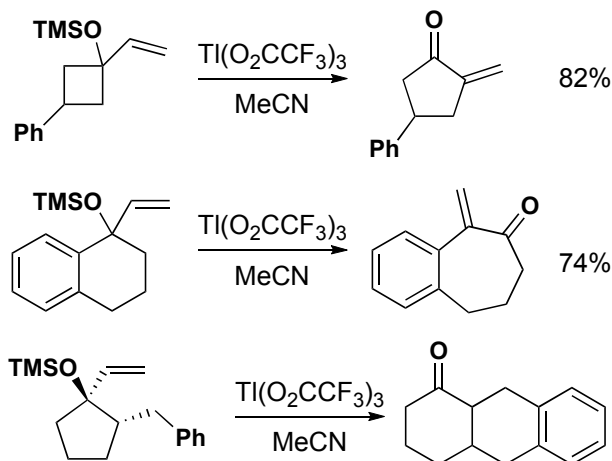
## To shift or to eliminate?

J. Chem. Soc., Perkin Trans. 1 1992, 2565



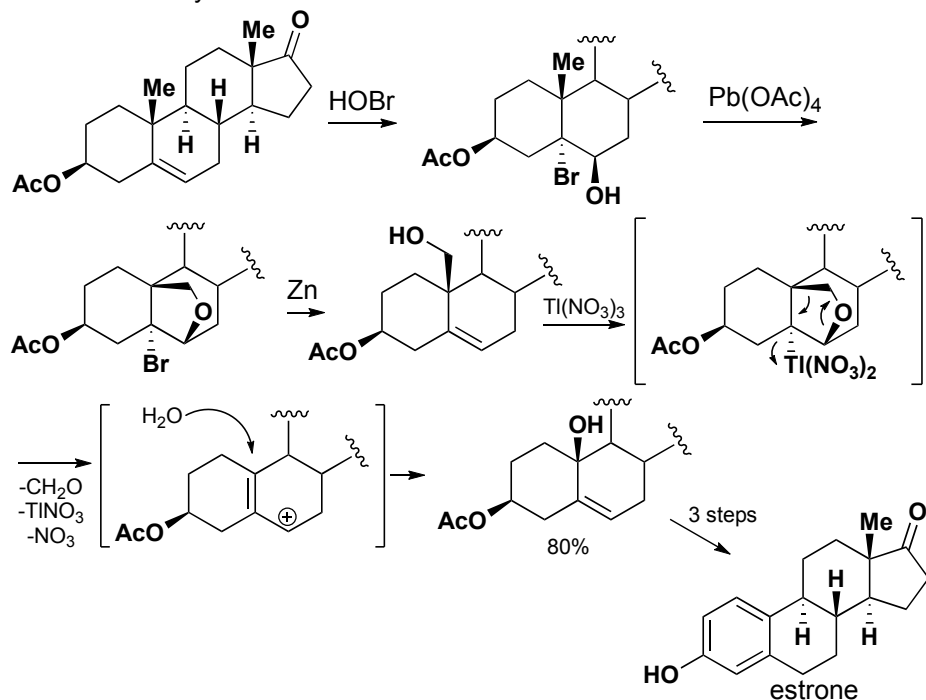
## Ring expansion

Tet. Lett. 1996, 3865

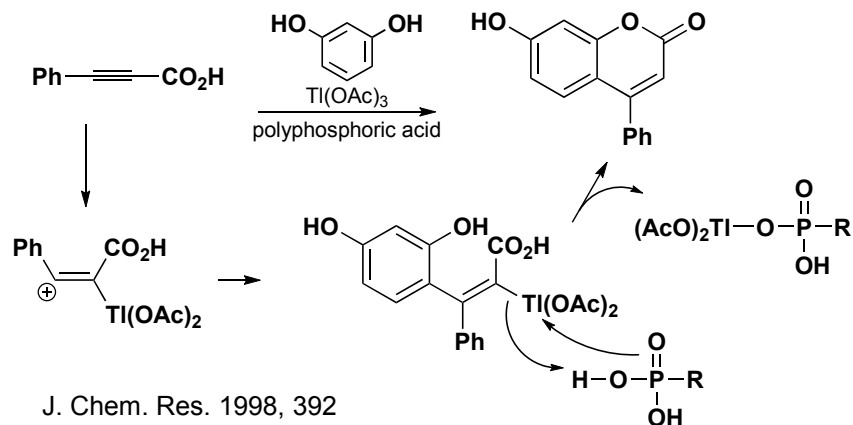


## Estrone semisynthesis

JOC 1994, 5439

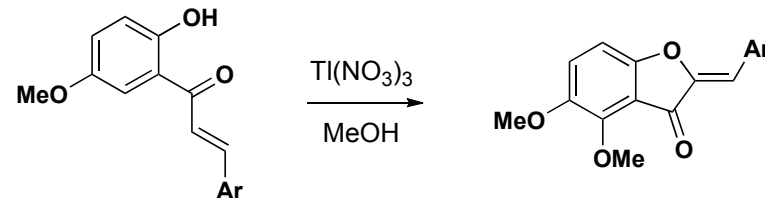


Olefins and alkynes react with Tl(III) with and without rearrangement, much like other pi-acids. Here is a one-pot synthesis of coumarins.

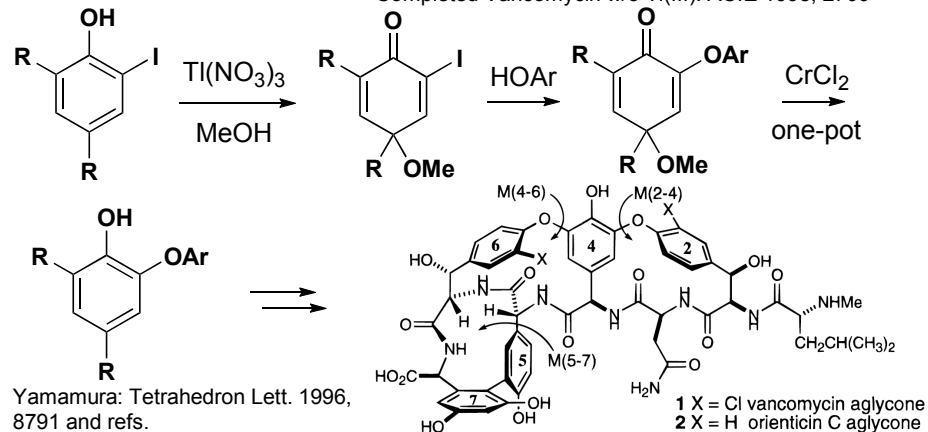


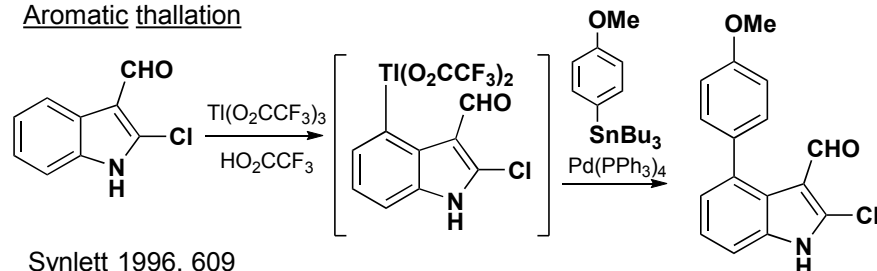
## Phenol oxidation.

JOC 1995, 6499

PhI(O<sub>2</sub>CCF<sub>3</sub>) does not activate the olefin, but it does do the other oxidation.

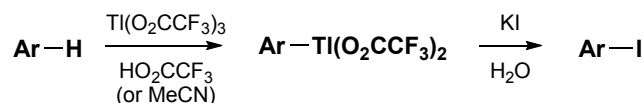
## Vancomycin syntheses

Evans: JACS 1997, 3419 and refs.  
Completed Vancomycin w/o Tl(III): ACIE 1998, 2700

Aromatic thallation

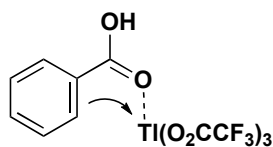
Synlett 1996, 609

## Thallation then halogenation

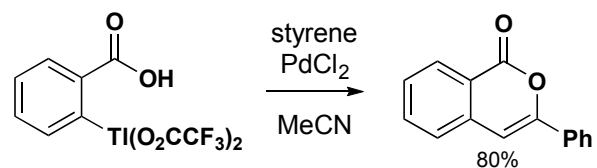


Tet. Lett. 1969, 2427

Substrate	Product	Yield
benzene	iodobenzene	96%
fluorobenzene	o:p = 11:89	70%
o-xylene	4-iodo-o-xylene	98%
anisole	o:p = 17:83	75%
benzoic acid	ortho only	96%
2-methylthiophene	2-methyl-5-iodothiophene	98%



## Thallation then Pd-coupling

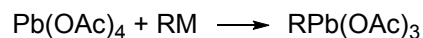
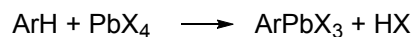


JACS 1984, 5274

Or you can do it with  
Ru, Cu, and alkynes:  
Org. Lett. 2012, 930.Not covered

One-electron aryl-aryl coupling

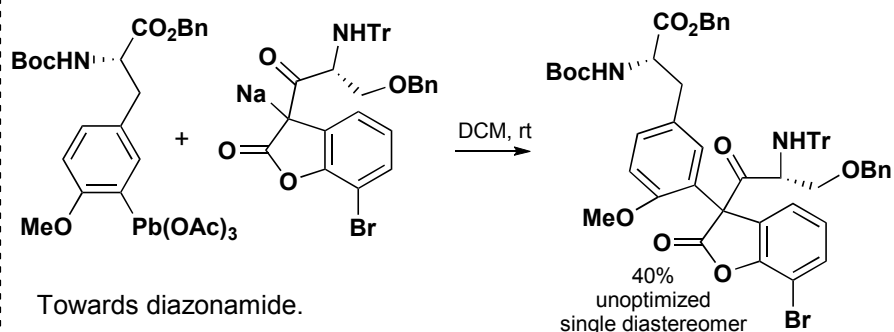
Triorganothallium and tetraorganothallate

Reductions with  $\text{Ti}^0$ LeadMaking lead reagents and making C-Pb bondsFor R = vinyl or alkynyl, M = Hg, Sn.  
For R = aryl, M = Si, Zn, B(OH)<sub>2</sub> are  
also used. Note: transfer with B(OH)<sub>2</sub>  
requires Hg(OAc)<sub>2</sub> as catalyst.

Ar must be electron-rich

X = OAc, O<sub>2</sub>CCF<sub>3</sub>Arylation and vinylation of enolates

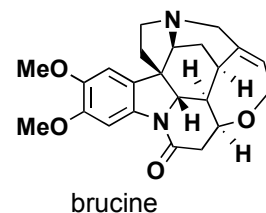
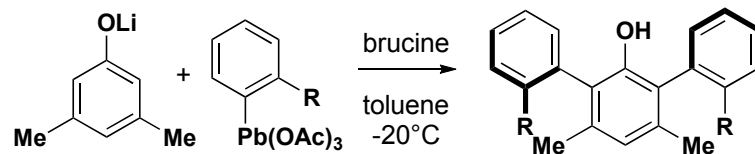
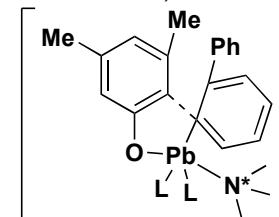
Synlett 1996, 609. Tetrahedron 2001, 5683.



Towards diazonamide.

## Enantioselective arylation of phenols

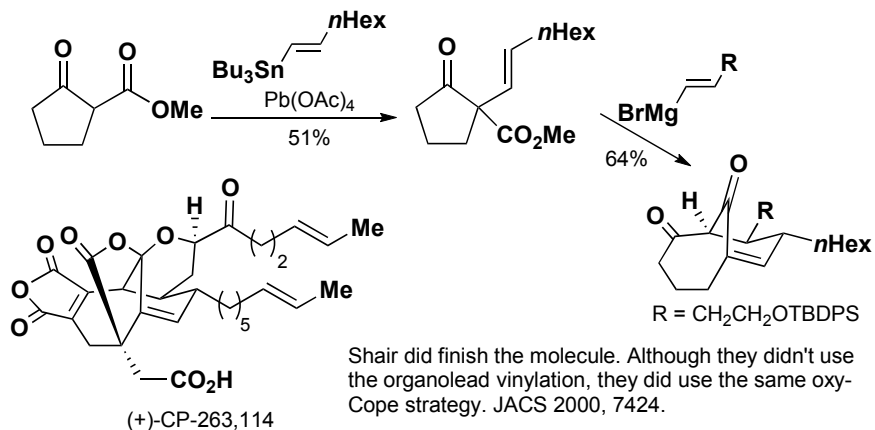
Yamamoto: JACS 1999, 8943

R = *i*Pr 99%, >99% de, 61% ee  
R = Ph 68%, >99% de, 83% eeAttempts to make the same C-C bonds, much less enantioselectively, gave lower yields for  
Pd-catalysis and no triaryl for Ni-catalysis.



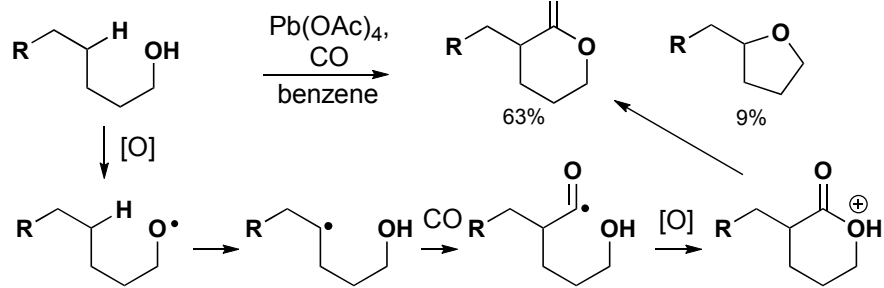
Enolate vinylation towards CP-263,114

Shair: JACS 1998, 10784

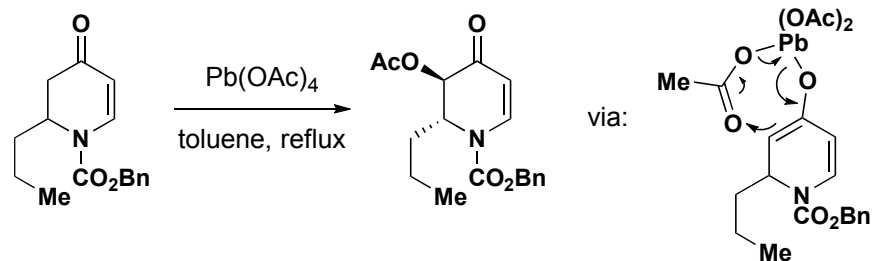
More functionalization through radical intermediates

Carbonylation of saturated alcohols

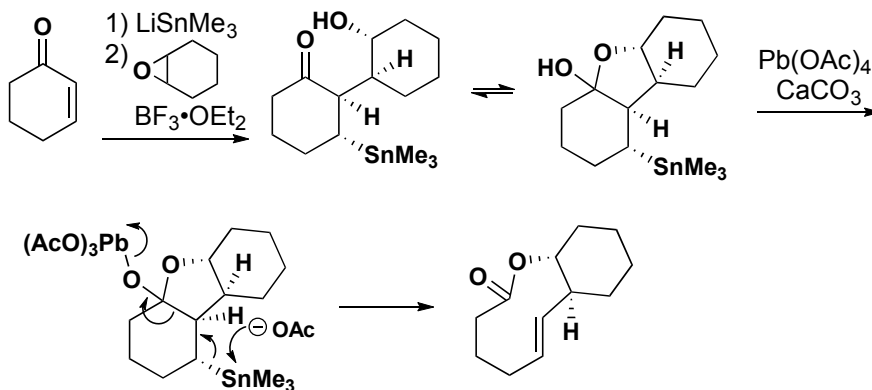
JACS 1998, 8692

α-oxidation of carbonyls

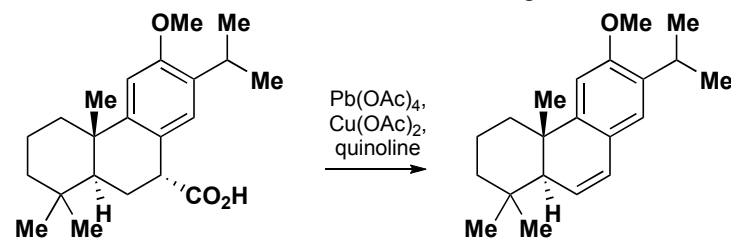
Tet. Lett. 1998, 5693

Oxidative cleavage of C-C bonds

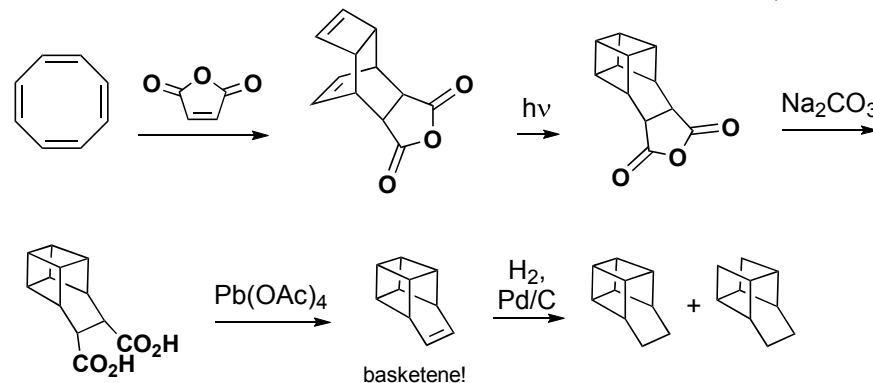
Tet. Lett. 2000, 9655



Bioorg. Med. Chem. 2001, 347



Tet. Lett. 1966, 1017



It should be pointed out that more effective structural design of lead species would be possible if one could control the number of coordination sites and complex ligand exchange. Carboxylate ligands are labile and rapidly undergo intermolecular exchange. In connection with this undesirable equilibrium, concomitant formation of oligomeric or polymeric structures as a result of complex intermolecular interactions imposes significant limitations on further development in this area of research.

-Taichi Kano and Susumu Saito, 2004

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#### Not covered

Pb(II) as a Lewis acid.

N-arylation (lead version of a Buchwald reaction)

Olefin aziridination

Carbon radicals from organolead species

Alkylation of aldehydes with tetraorganolead species

Allylic and benzylic acetoxylation

Pb(0) reductions