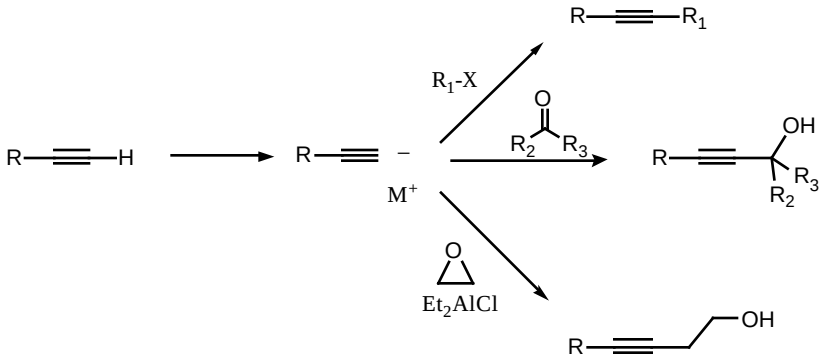
C≡C Bond Formation

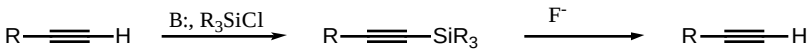
1. From other acetylenes
2. From carbonyls
3. From olefins
4. From Strained Rings
5. Eschenmosher Fragmentation
6. Allenes

From Other Acetylenes

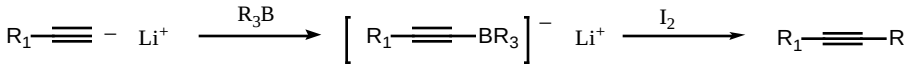
- The proton of terminal acetylenes is acidic (pK_a= 25), thus they can be deprotonated to give acetylide anions which can undergo substitution reactions with alkyl halides, carbonyls, epoxides, etc. to give other acetylenes.



- Since the acetylenic proton is acidic, it often needs to be protected as a trialkylsilyl derivative. It is conveniently deprotected with fluoride ion.

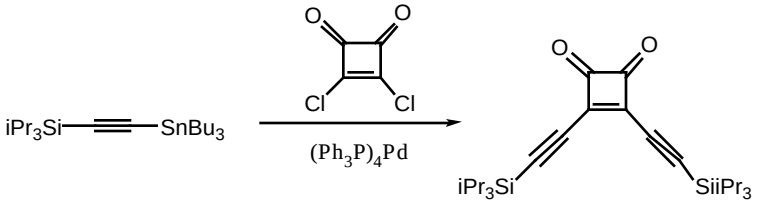


Acetylide anions and organoboranes

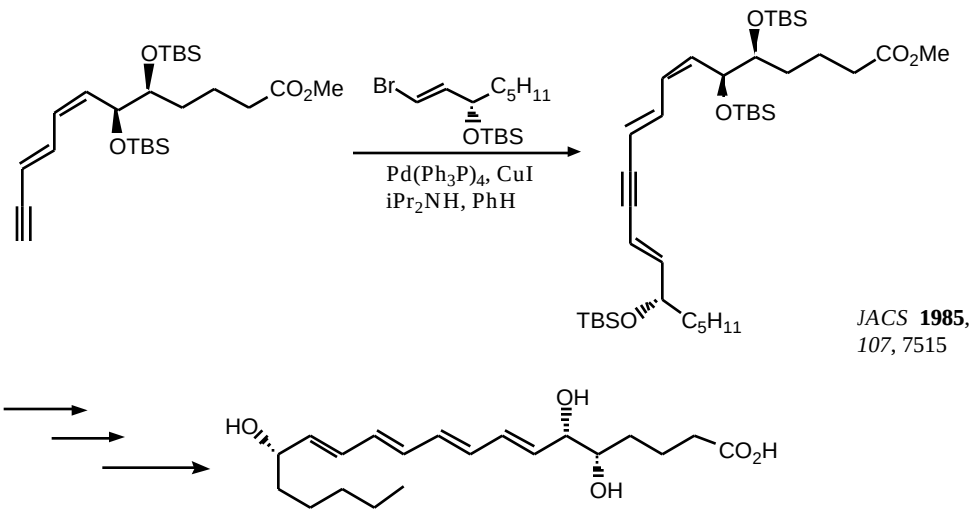


JOC **1974**, *39* , 731
JACS, **1973**, *95* , 3080

Palladium Coupling Reactions:

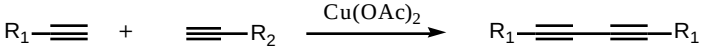


JACS **1990**, *112*, 1607



JACS **1985**, *107*, 7515

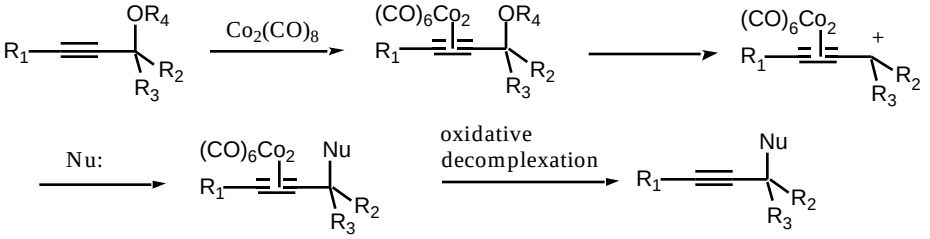
Copper Coupling- 1,3-diynes

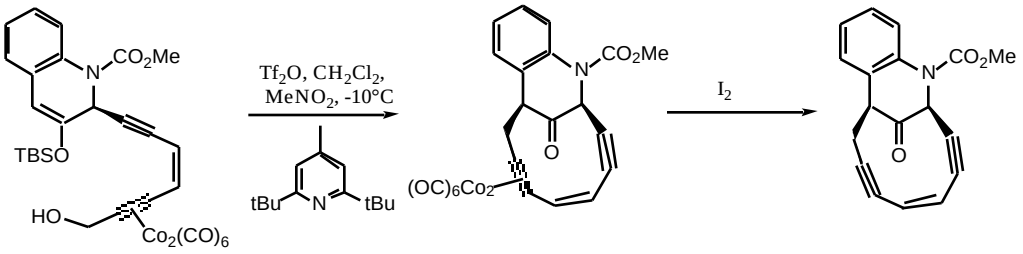


Adv. Org. Chem. **1963**,*4* , 63

Nicholas Reaction

- acetylenes as their $Co_2(CO)_8$ complex can stabilize an α-positive charge, which can subsequently be trapped with nucleophiles.

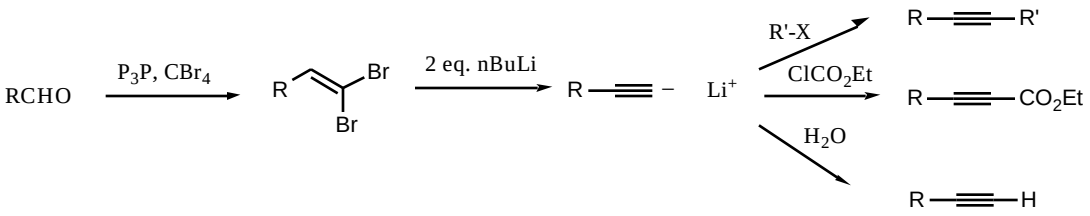


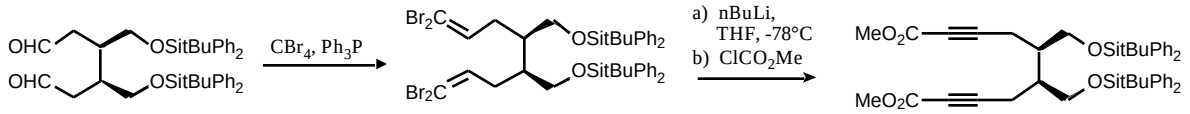


JCSCC **1991**, 544

$Co_2(CO)_6$-acetylene deocomplexation: *JOC* **1997**, *62*, 9380

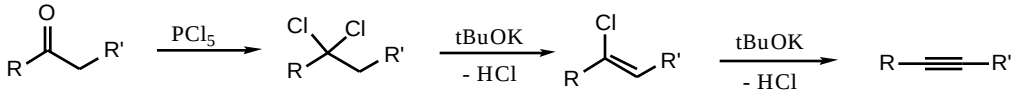
From Aldehydes and Ketones



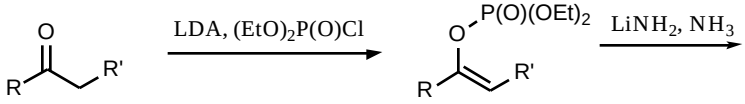


JACS **1992**, *114* , 7360

- by conversion of ketones to gem-dihalides followed by elimination

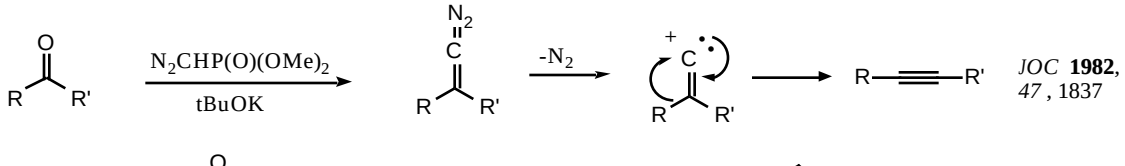


- by conversion of ketones to enol phosphates followed by elimination

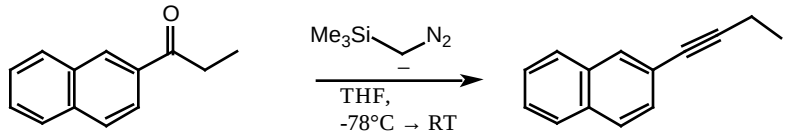


JOC **1987**, *52* , 4885

- Insertion reaction of a vinyl carbene (terminal acetylenes)



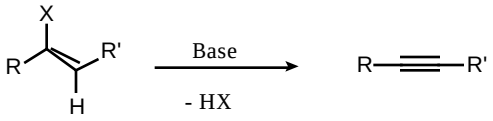
JOC **1982**, *47* , 1837



Synlett **1994**, 107

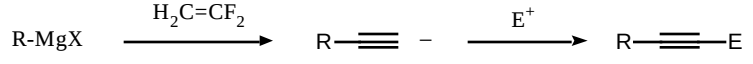
Via Elimination Reactions of Vinyl Halides

- Treatment of vinyl halides with strong base gives acetylenes.



X= Cl, Br, I, OTf, O_3SR, $OP(O)R_2$ Base= LDA; tBuOK; $NaNH_2$, DBU

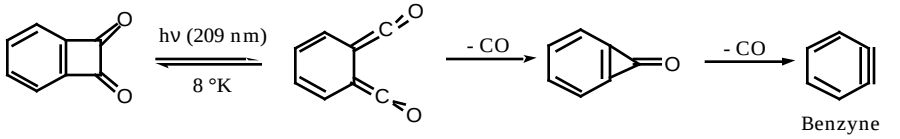
- Addition of Grignard reagents to 1,1-difluoroethylene yields an acetylide anion which can be subsequently trapped with electrophiles.



TL **1982**, *23* , 4325
JOC **1976**, *41* , 1487

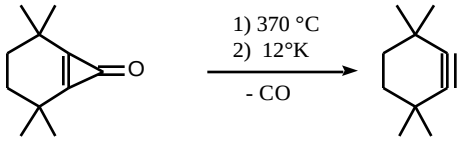
Strained Rings *Topics in Current Chemistry* **1983**, *109*, 189.

- Cyclopropenones and cyclobutendiones can be photolyzed or thermolyzed (FVP) to give acetylenes.

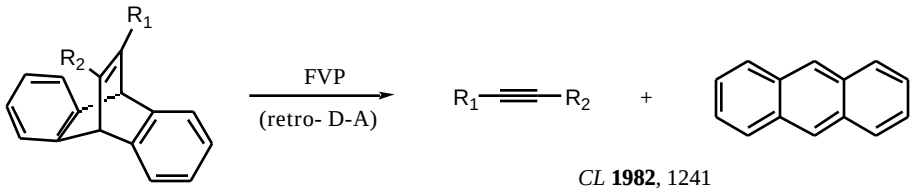


JACS **1973**, *95* , 6134

Benzyne

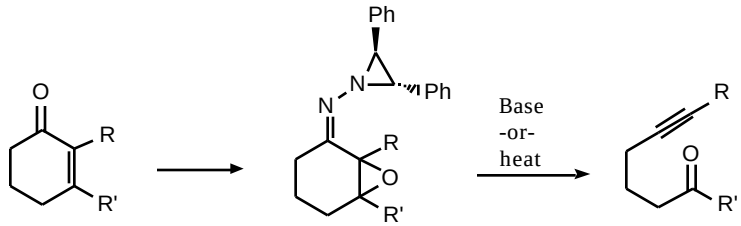


ACIEE **1988**,*27* , 398
JACS **1991**, *113* , 6943

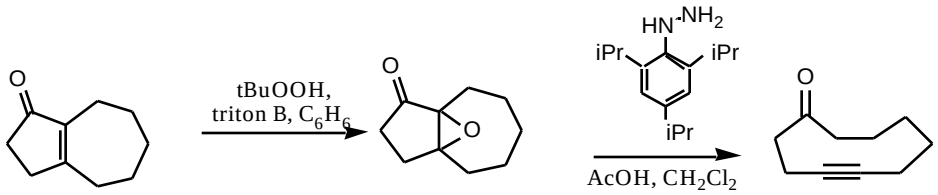


CL **1982**, 1241

Eschenmoser Fragmentation



HCA **1972**, *55* , 1276

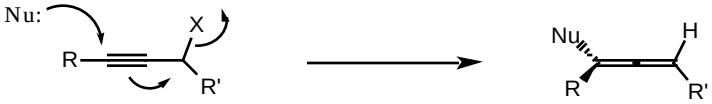


JOC **1992**, *57*, 7052

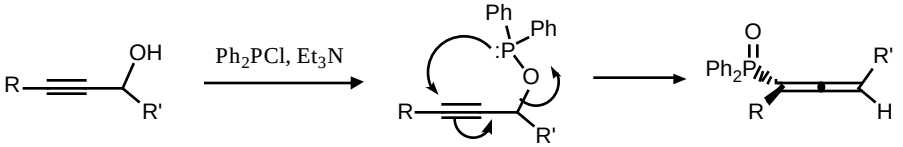
Allenes *Tetrahedron* **1984**, *40*, 2805

- from dihalocyclopropanes

- From SN2' Reactions



- from sigmatropic rearrangements from propargyl sulfoxides and phosphine oxides.



TL **1990**, *31* , 2907
JACS **1990**, *112* , 7825