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Levin Group Meeting
University of Chicago
November 4, 2020

# Overview

This day in history

Woodward and Hoffman: Orbital Symmetries in Concerted Cycloaddition Reactions and Sigmatropic Rearrangements

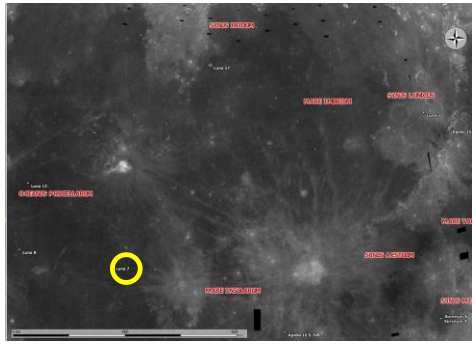
Wehry and Rogers: LFER of Electronically Excited States

Closs and Coyle: Halogenation of Diazomethane

Graham: Halogenation of Amidines

Dolfini and Simpson: Enamine Cycloaddition with N-Carbethoxyaziridine

# This Day (Month) in History



*October 4*
*USSR launches Luna 7, which crash lands on the Moon*

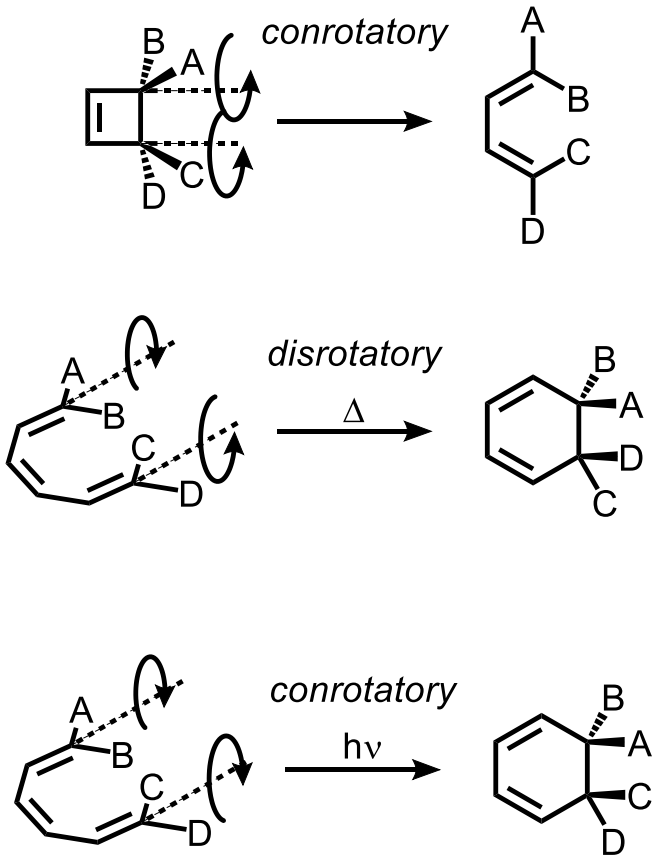

*October 9*
*Beatles' "Yesterday" goes #1 and stays for 4 weeks*

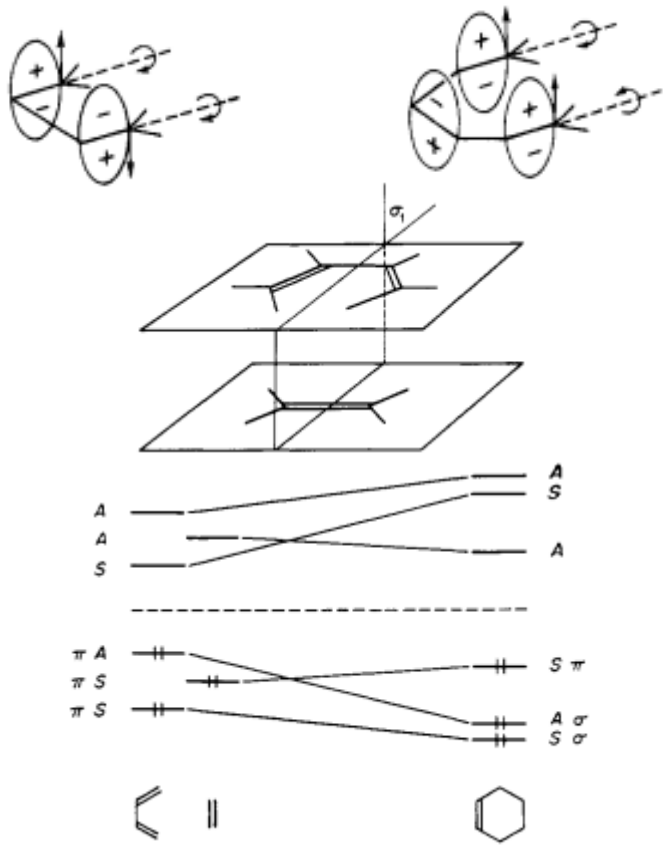
*October 21*
*Robert B. Woodward awarded Nobel Prize in Chemistry*

*October 5*
*Charles Linster performs 6006 consecutive push ups*


*October 1, 8, 29*
*France, USSR, and US perform nuclear tests*

# Woodward-Hoffman Rules



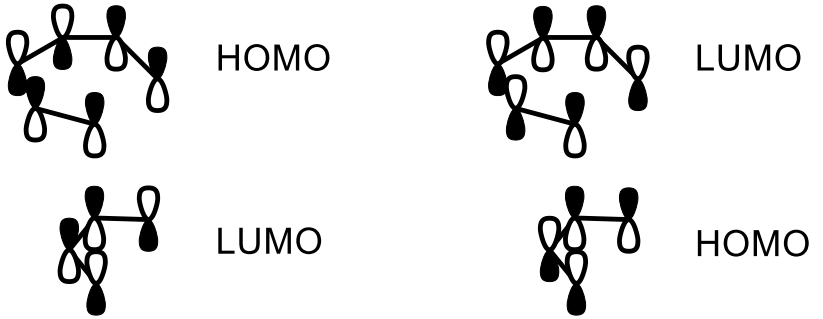




R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965); R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.* 1965, 87, 19, 4388–4389; R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.* 1965, 87, 19, 4389–4390

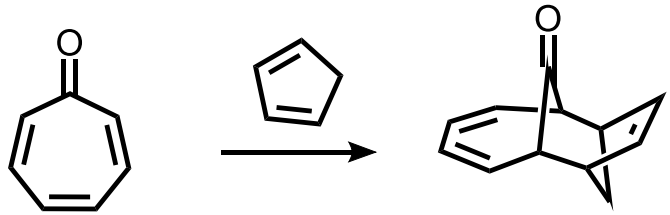
# Application to Concerted Cycloadditions


*Either way, endo is preferred*

*preferred* *not preferred*

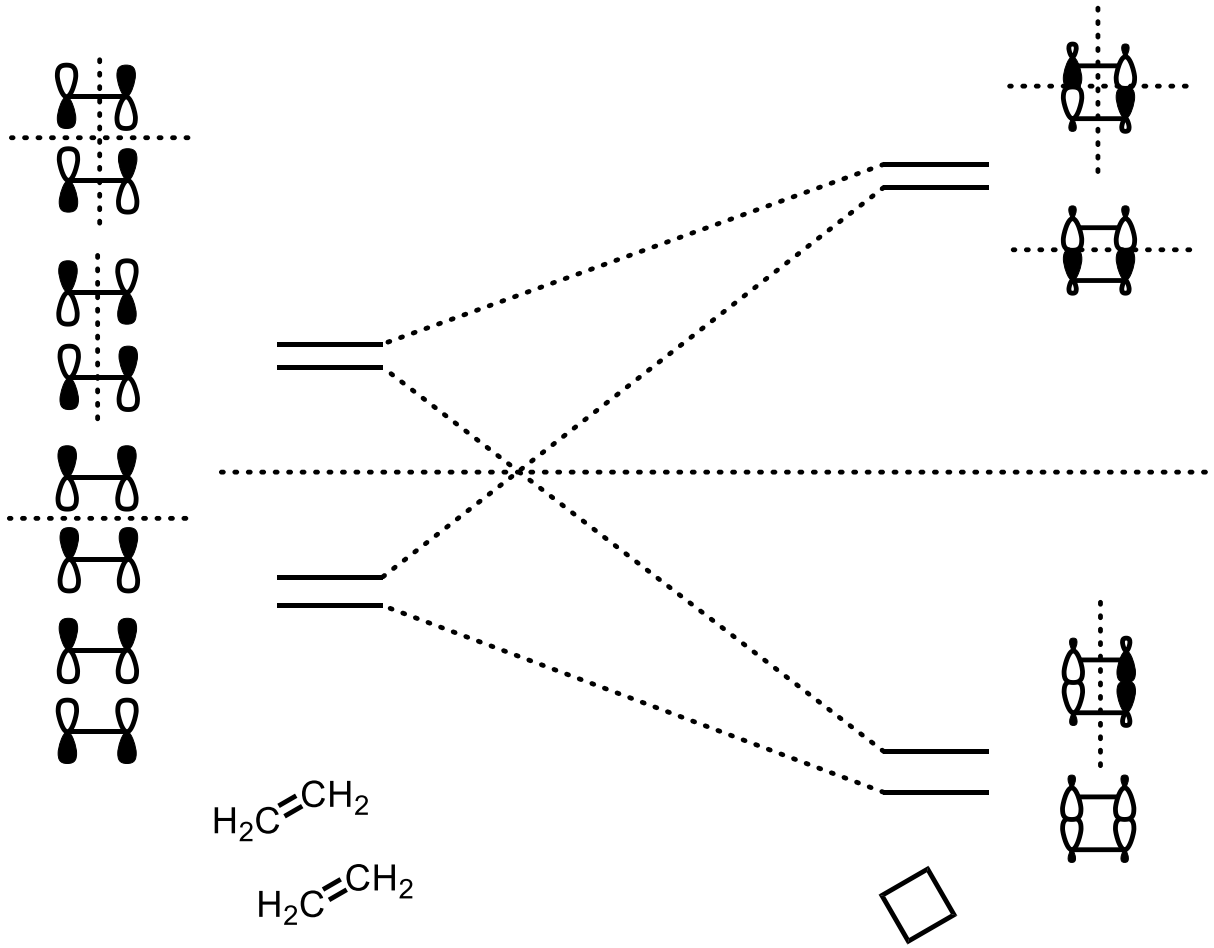



*exo should be preferred*




*exo [6+4]*

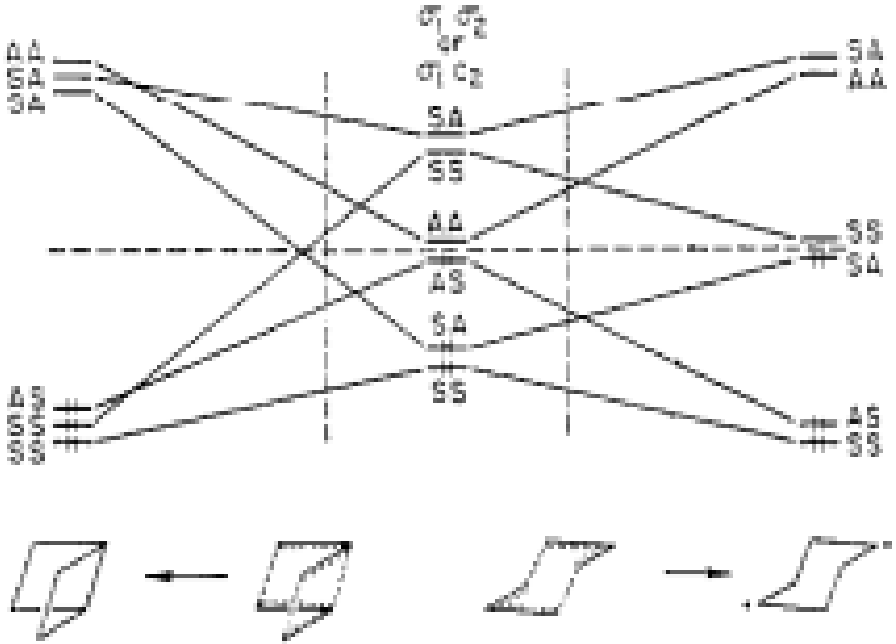
# Correlation Diagrams Provide Visual




*Correlation diagram predicts disallowed thermal [2+2]*

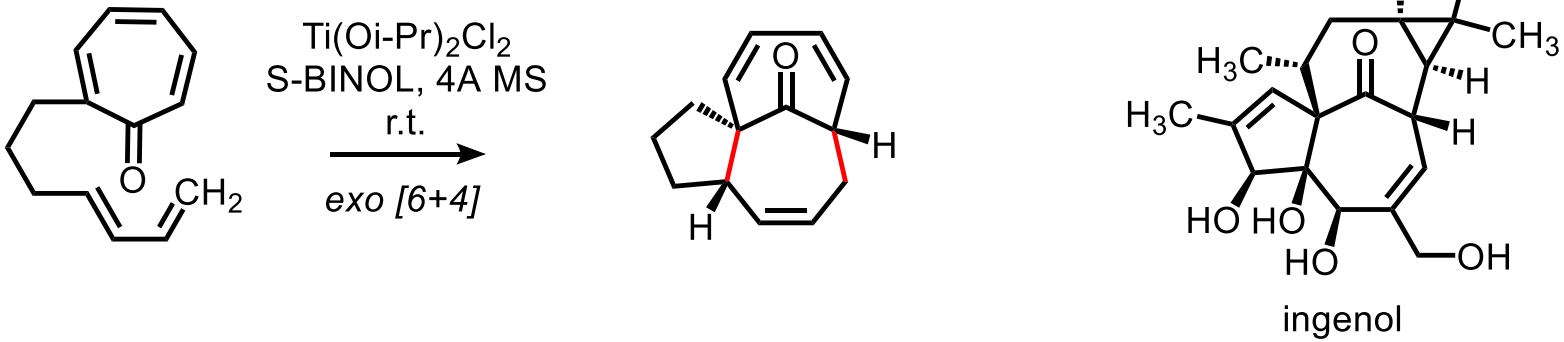
R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965); R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.* 1965, 87, 19, 4389–4390

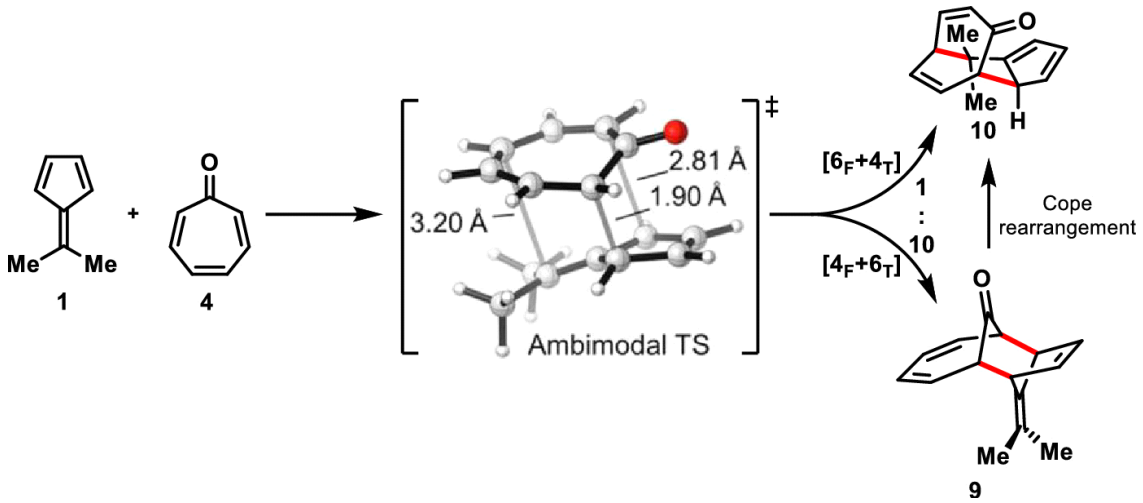
# Application to Sigmatropic Rearrangements



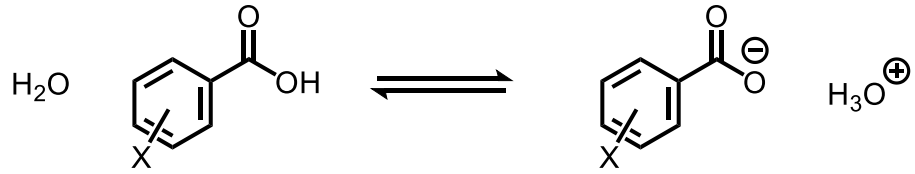
*Predicts small preference for chair-like T.S. in Cope rearrangement*

# Extension to Higher Order Systems



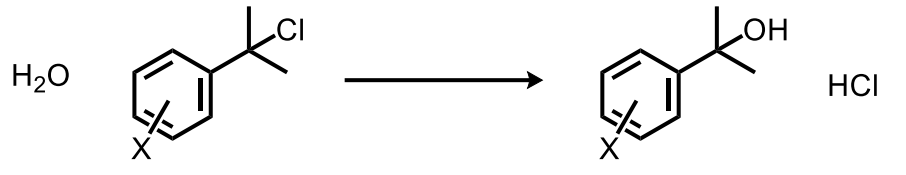



# Linear Free Energy Relationships (LFER)



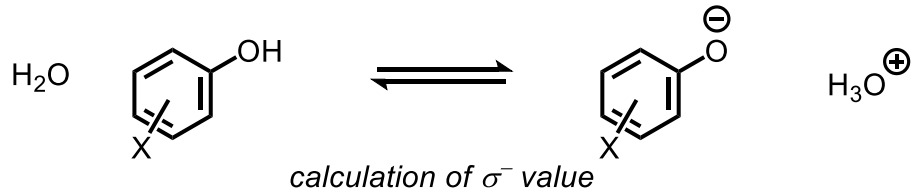

*calculation of $\sigma$ value*

Hammett, *Chem. Rev.* 1935, 17, 1, 125–136




*calculation of $\sigma^{+}$ value*

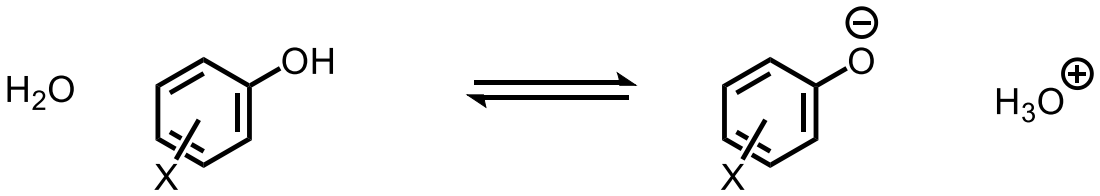
Brown, *J. Am. Chem. Soc.* 1958, 80, 18, 4979–4987

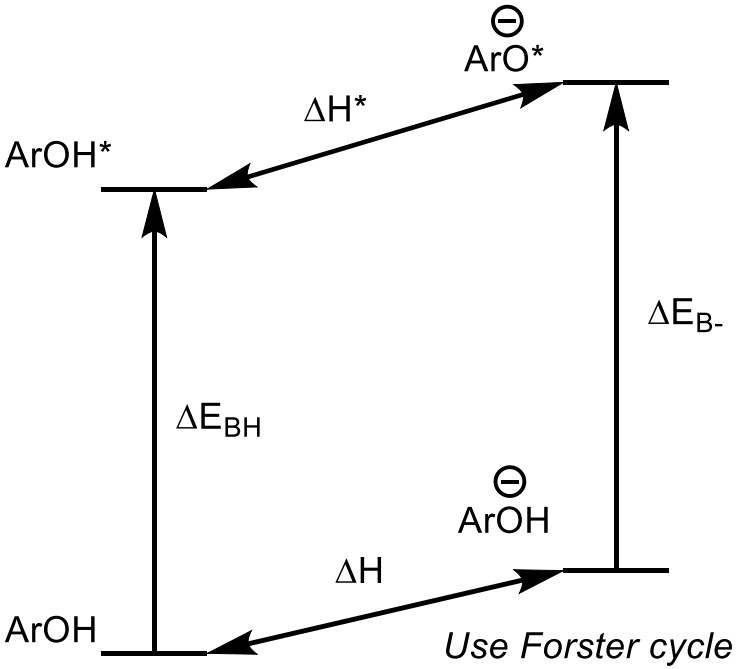



*calculation of $\sigma^{-}$ value*

Jaffe, *Chem. Rev.* 1953, 53, 2, 191–261

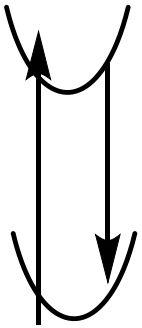
# LFER in Excited State Phenols



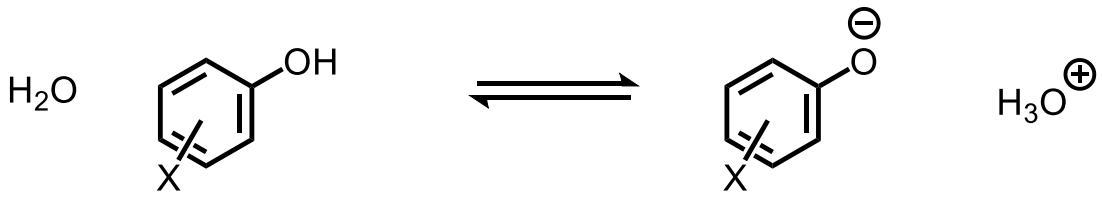

*Use Forster cycle to determine excited state pKa*

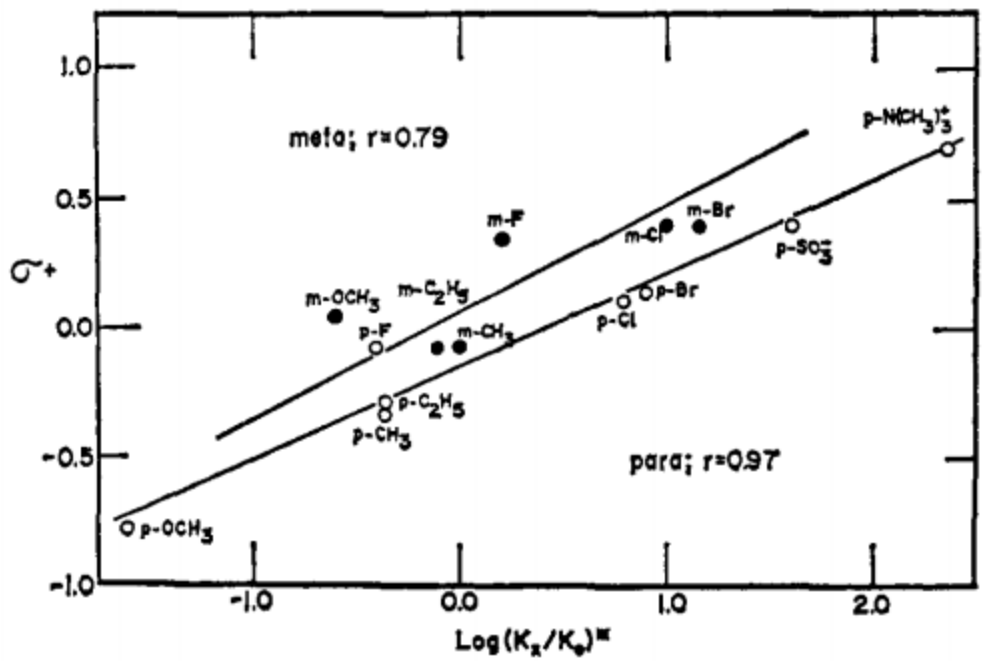
Assumptions:
1. DS is the same in ground and excited states
2. Need to know where 0-0 transition is
3. Absorption bands of the conjugate acid-base pair are similar



*Average frequencies of absorption and fluorescence maximum*

# LFER in Excited State Phenols



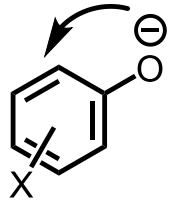




*Phenols are much more acidic in the excited state*

*Resonance plays a relatively larger role in excited state*

*Analysis didn't work for triplet states because of uncertainties in determination of frequencies*

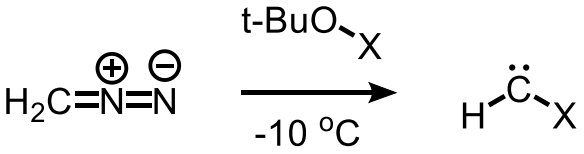
*Nature of the effect:*



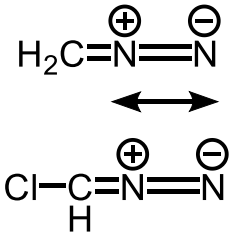

*increased charge transfer in the excited state*

*J. Am. Chem. Soc.* 2000, 122, 49, 12243–12253

# Halogenation of Diazomethane

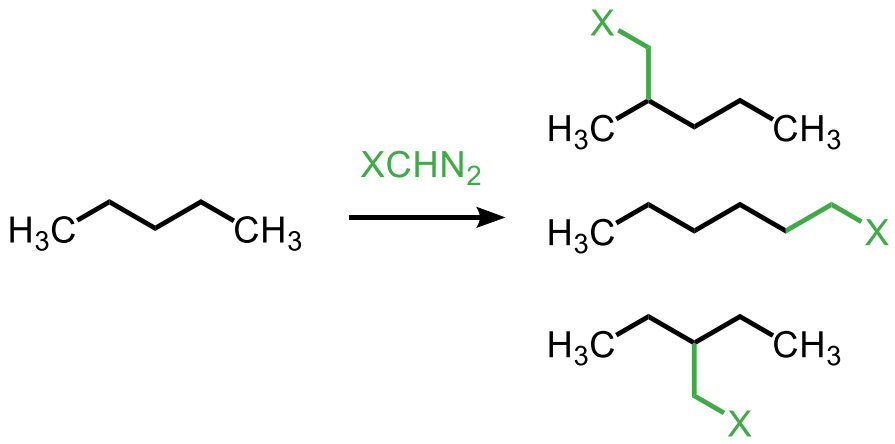


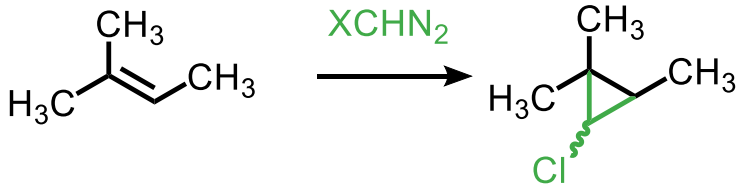

*spectroscopic evidence*




N=N Stretch at -60 °C
shifts by 30 cm-1

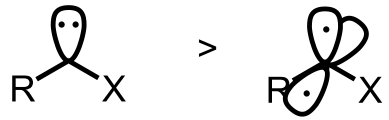
*chemical evidence*



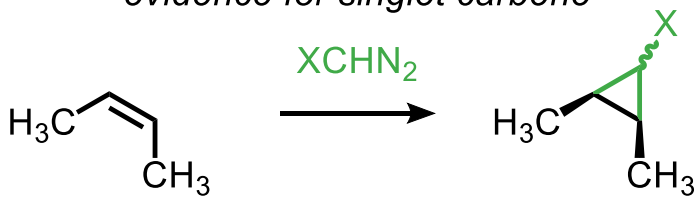



# Halocarbene Reactivity

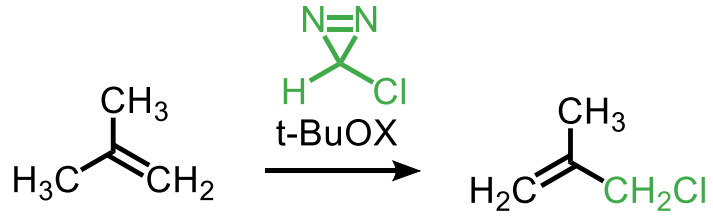
*π donation from R and X promotes singlet carbene*

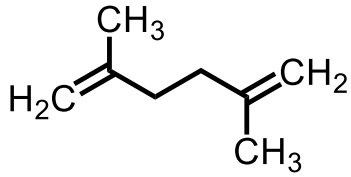



*stereospecificity indicates concerted addition, evidence for singlet carbene*

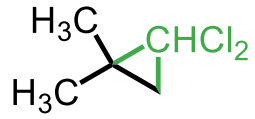


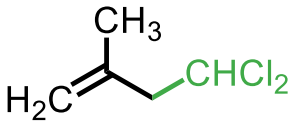

*evidence for dihalocarbenes*



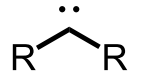

*radical inhibitors increase yield of cyclopropane*



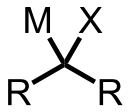




major $C_5$ product

# Carbenoid Reactivity

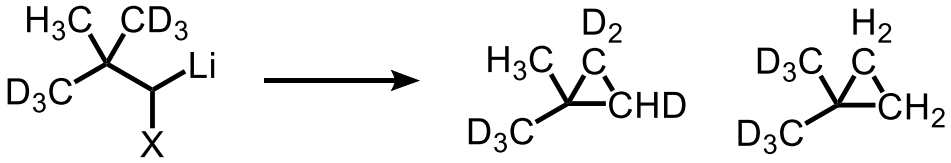



*carbene*

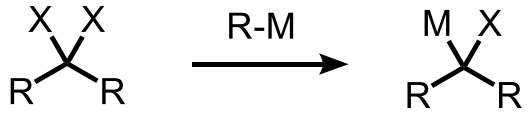



*carbenoid*

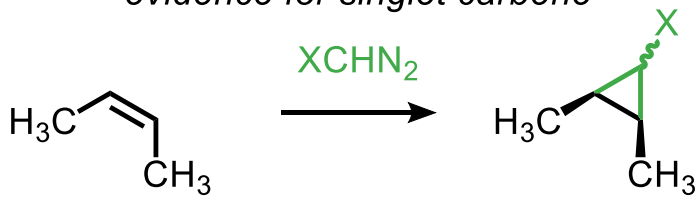
*carbenoids can also be electrophilic*

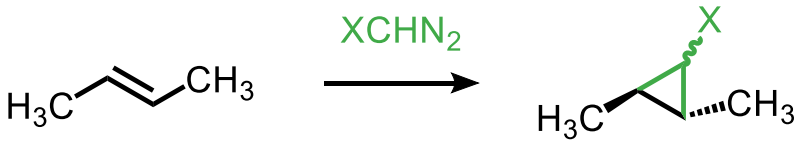


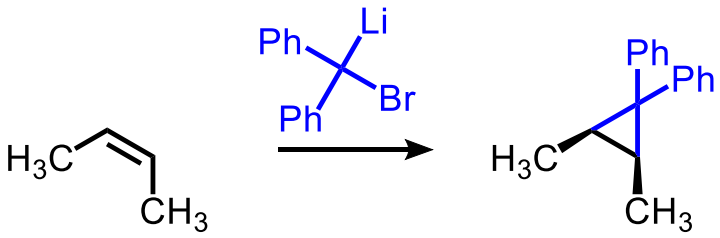

*carbenoid synthesis*




*stereospecificity indicates concerted addition, evidence for singlet carbene*

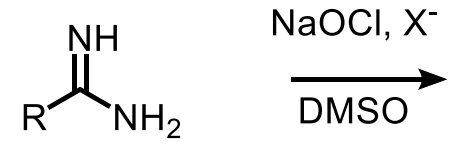


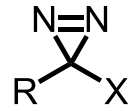

*... or carbenoid*

# Halogenation of Amidines

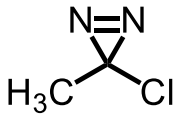


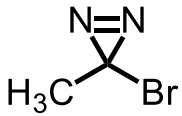

NaOCl, $X^-$

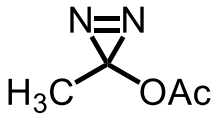
DMSO

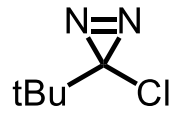


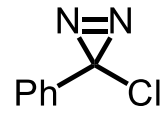

*scope*

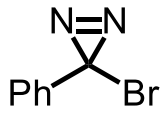


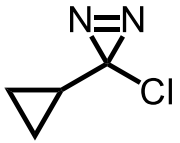



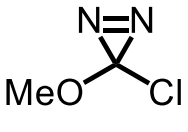



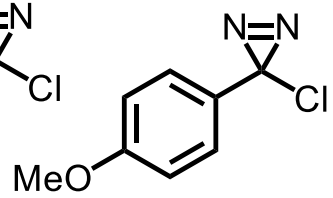



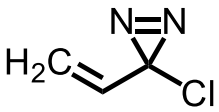



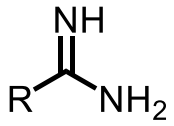



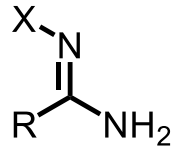



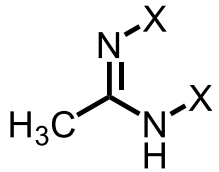

*proposed mechanism*



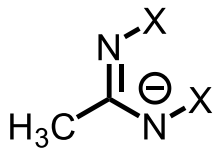

NaOX

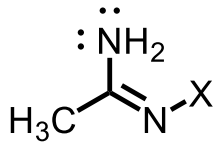


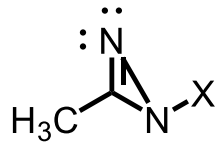

NaOX




KOH

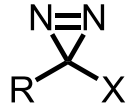


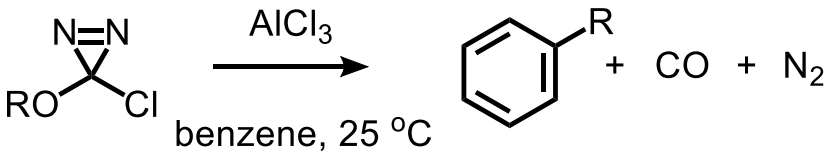


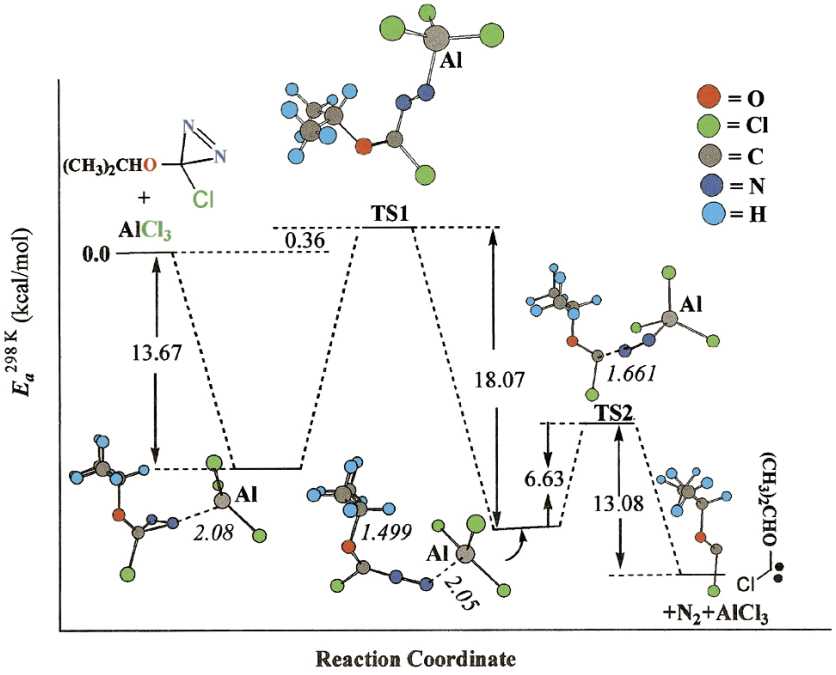
$X^-$



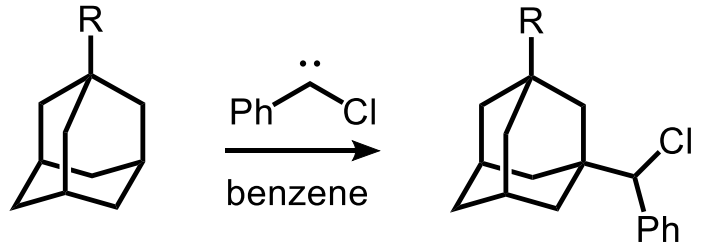
# Halogenation of Amidines

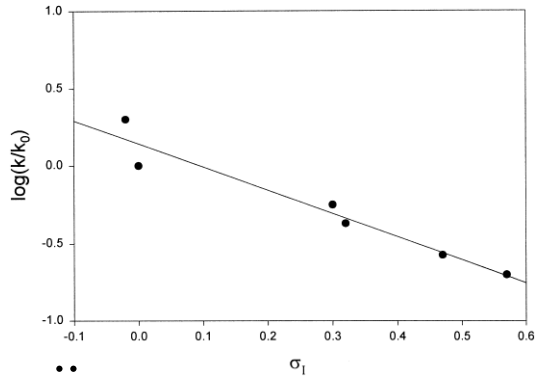
Moss et al., *J. Am. Chem. Soc.* 2000, 122, 40, 9878–9879

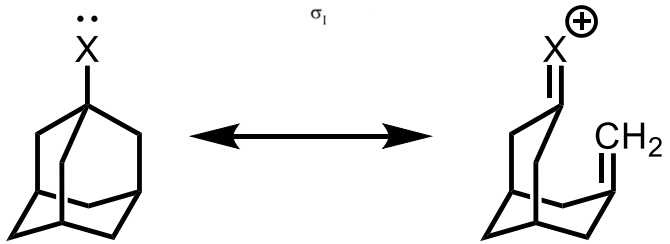


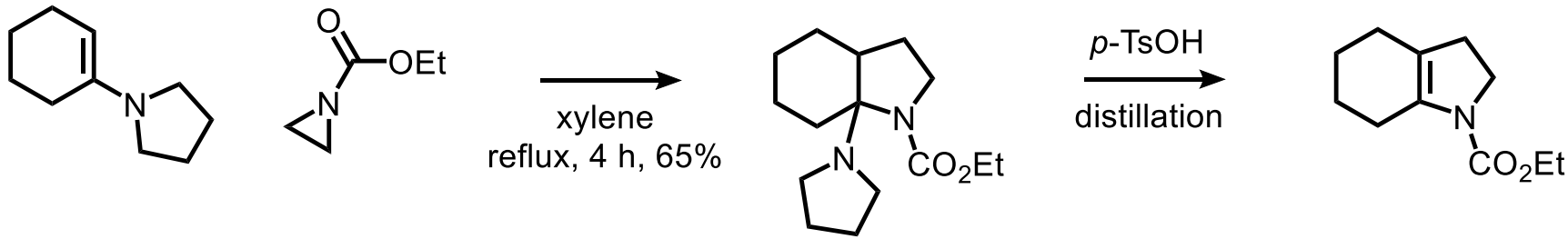

Moss and Yan, *Org. Lett.* 1999, 1, 5, 819–822



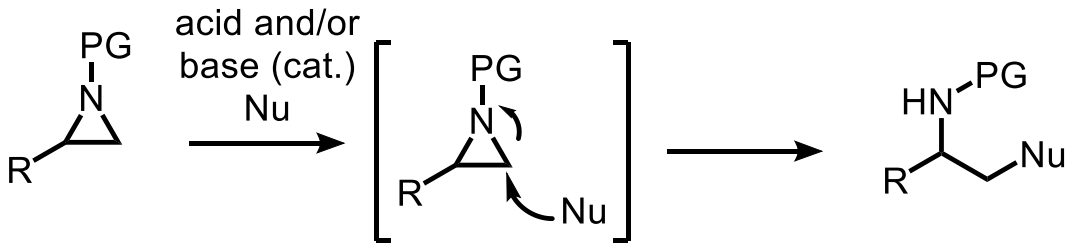



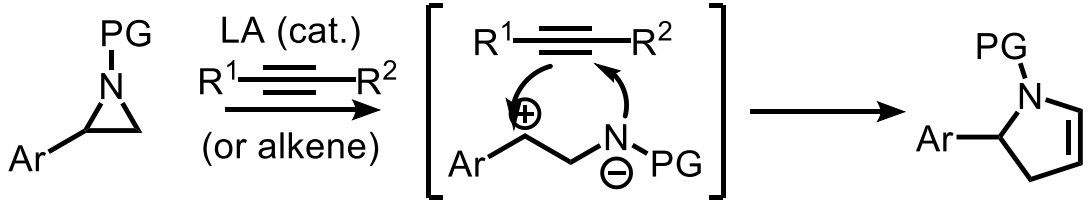



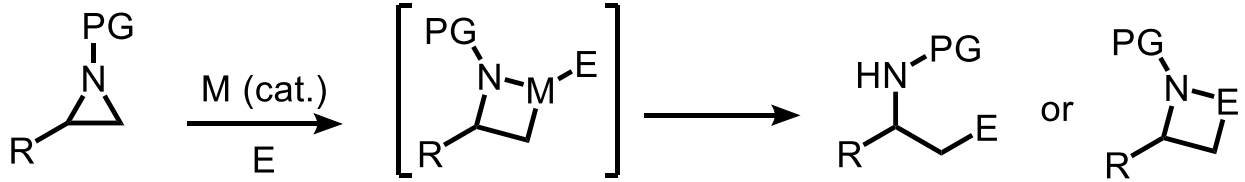
# Enamine Cycloaddition with N-carbethoxyaziridine



# Aziridine Activation




E = alkyl, aryl, CO, alkene, heterocumulene, etc.