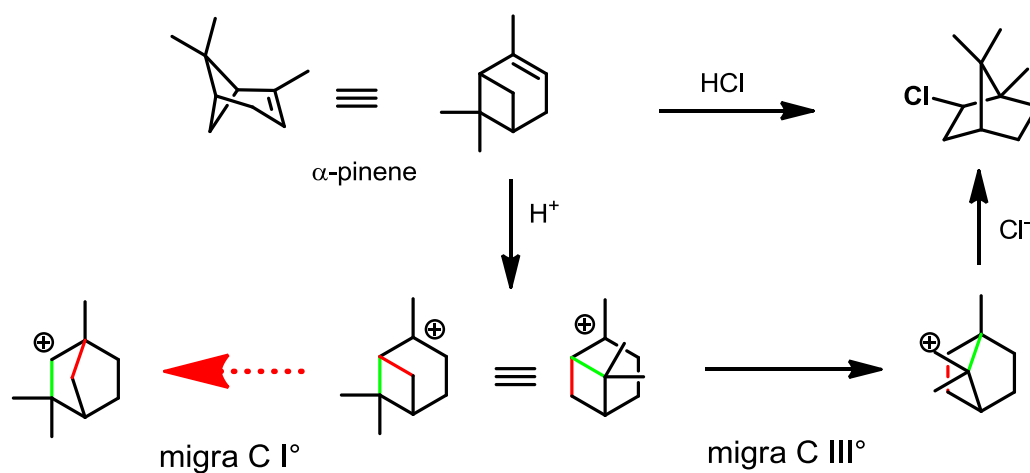
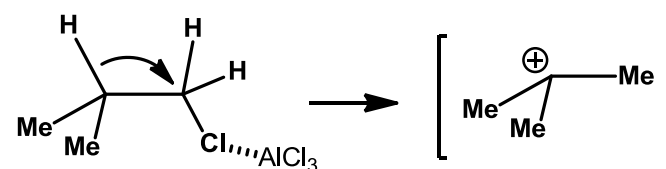
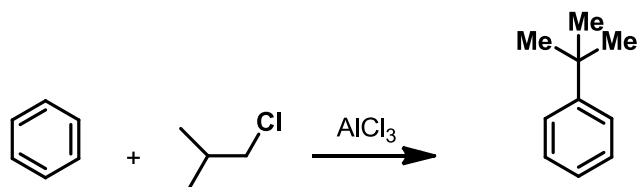
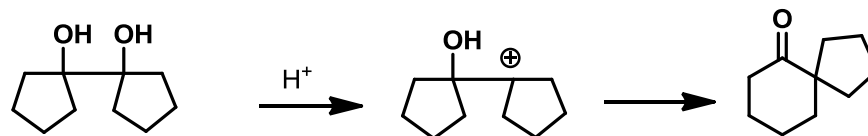
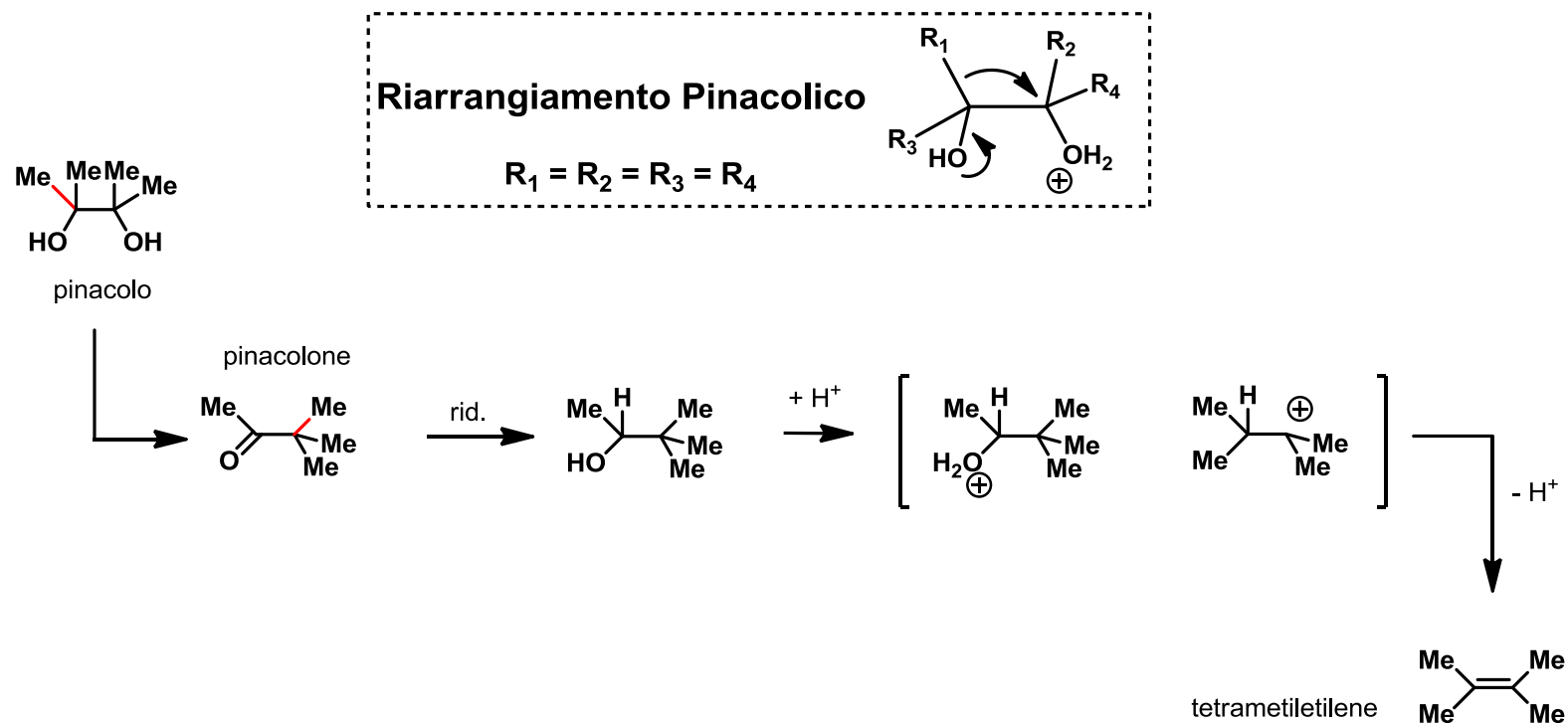


Georg (Egor) Egorovich Wagner (Vagner)
 29 November 1849 - 27 November 1903
 Russian, b. Kazan, Russia
Wagner-Meerwein rearrangement

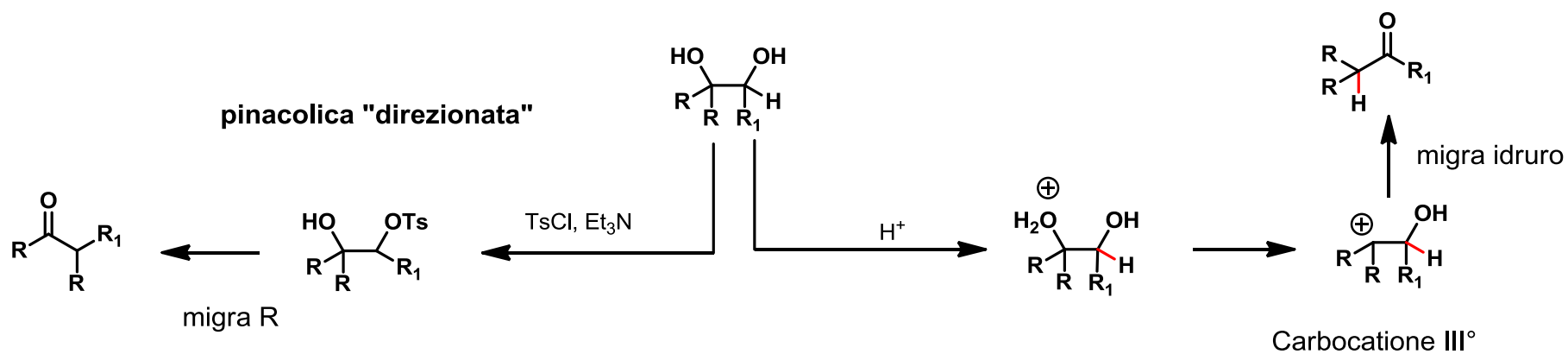
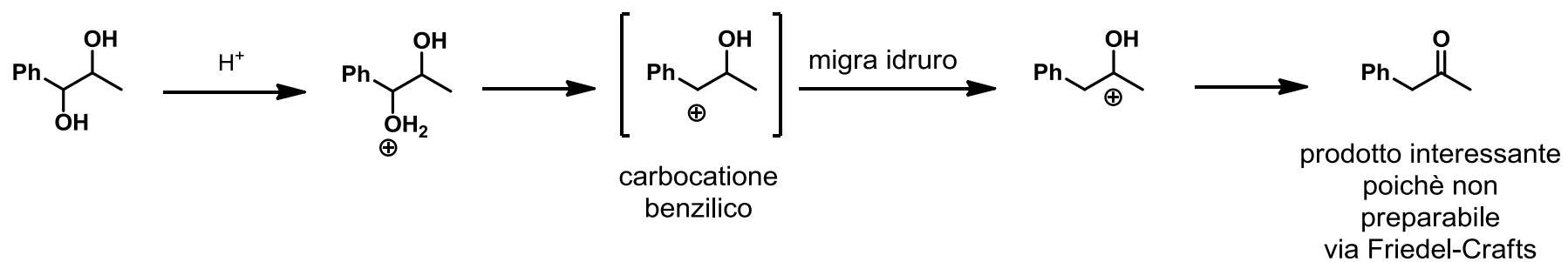
Hans Leberecht Meerwein
 30 May 1879 - 24 October 1965
 German, b. Hamburg, Germany

riarrangiamento 1,2 di carbocationi

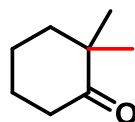
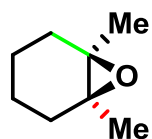
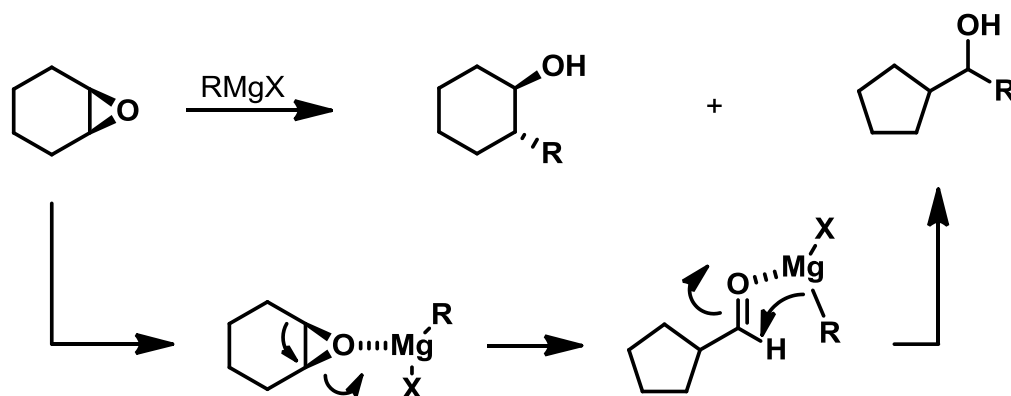
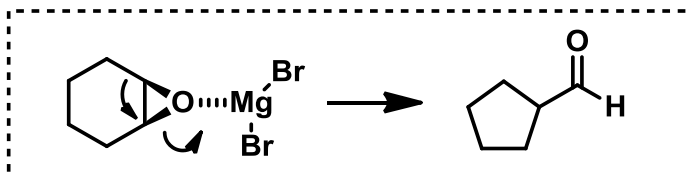




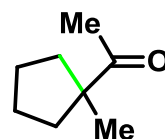
ma se non è $R_1 = R_2 = R_3 = R_4$??



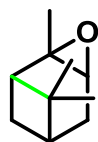
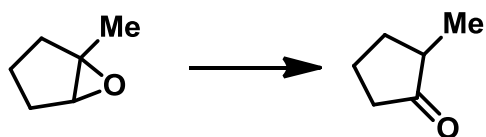
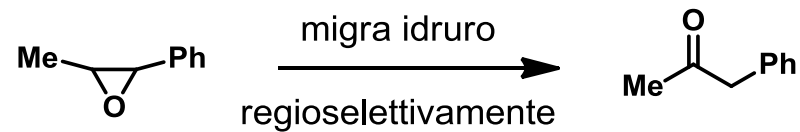
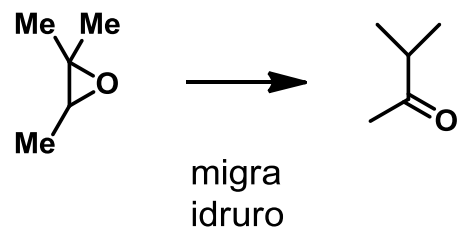
riarrangiamento 1,2 di epossidi *similpinacolic*



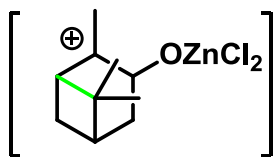
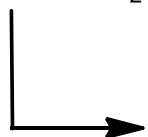
+



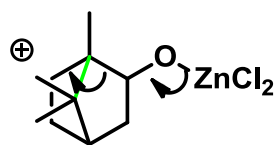
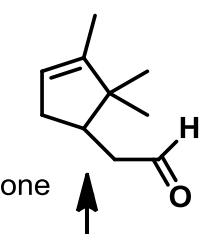
migra C I°
prodotto maggioritario



ZnCl₂



frammentazione
"push-pull"



Nikolai Jakovlevich Demjanov (Dem'anov, Demianov)

15 March 1861 - 19 March 1938

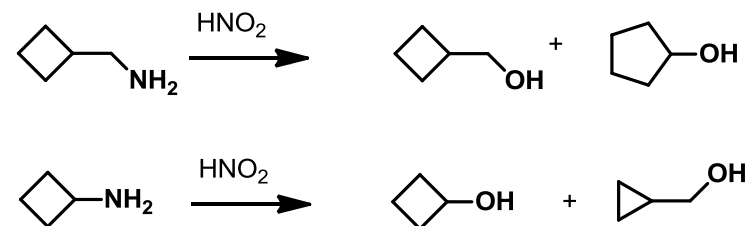
Russian, b. ?

Tiffeneau-Demjanov reaction

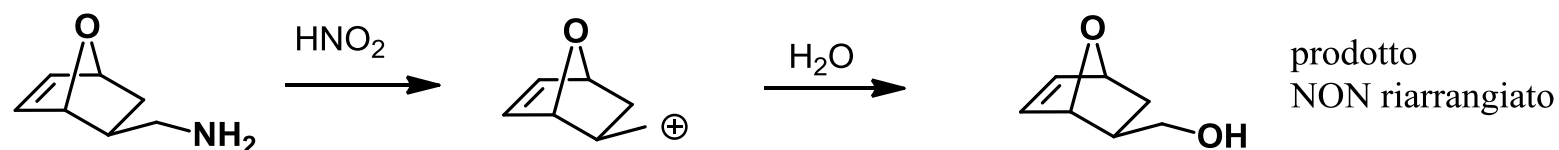
Tiffeneau, M.; Weill; Tschoubar, B., Compt. Rend. 1937, 205, 54

Demjanov rearrangement

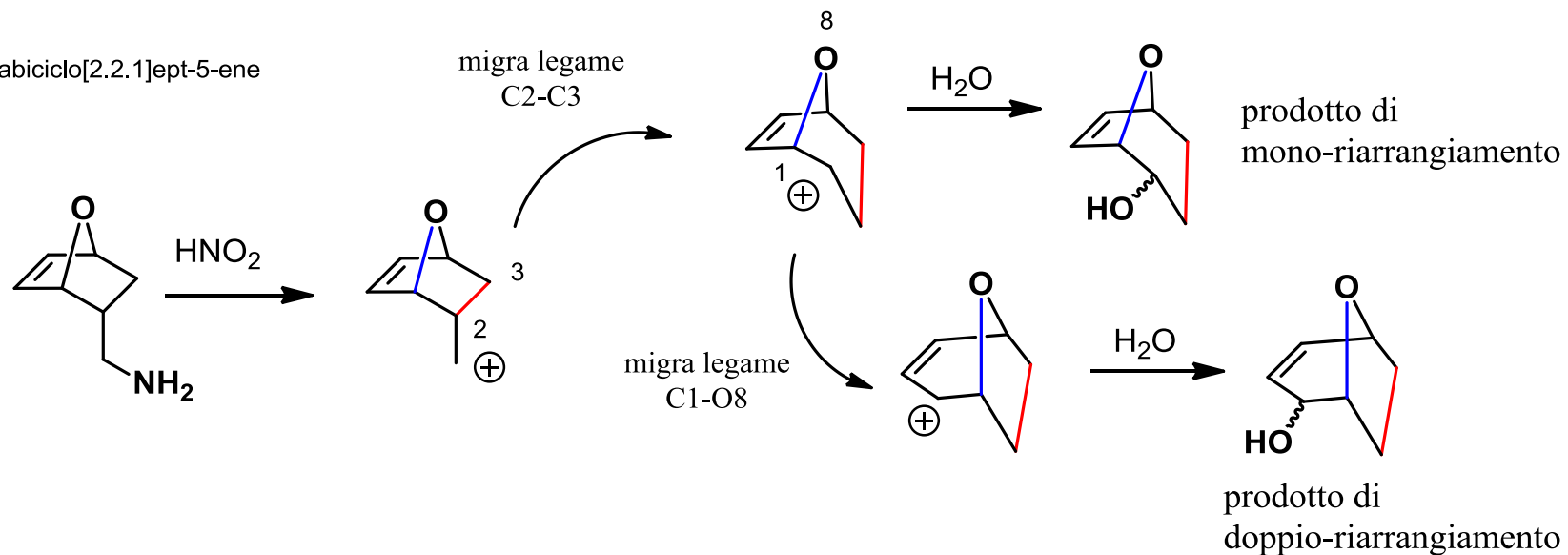
Demjanov, N.J.; Lushnikov, M., J. Russ. Phys. Chem. Soc. 1903, 35, 26



2-*exo*-aminometil-7-oxabicyclo[2.2.1]ept-5-ene



2-*endo*-aminometil-7-oxabicyclo[2.2.1]ept-5-ene

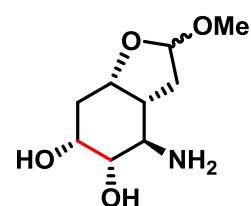


Marc Émile Pierre Adolphe Tiffeneau

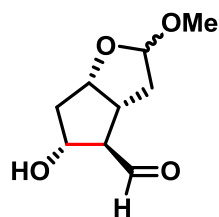
5 November 1873 - 20 May 1945

French, b. Mouy, France

Tiffeneau-Demjanov rearrangement

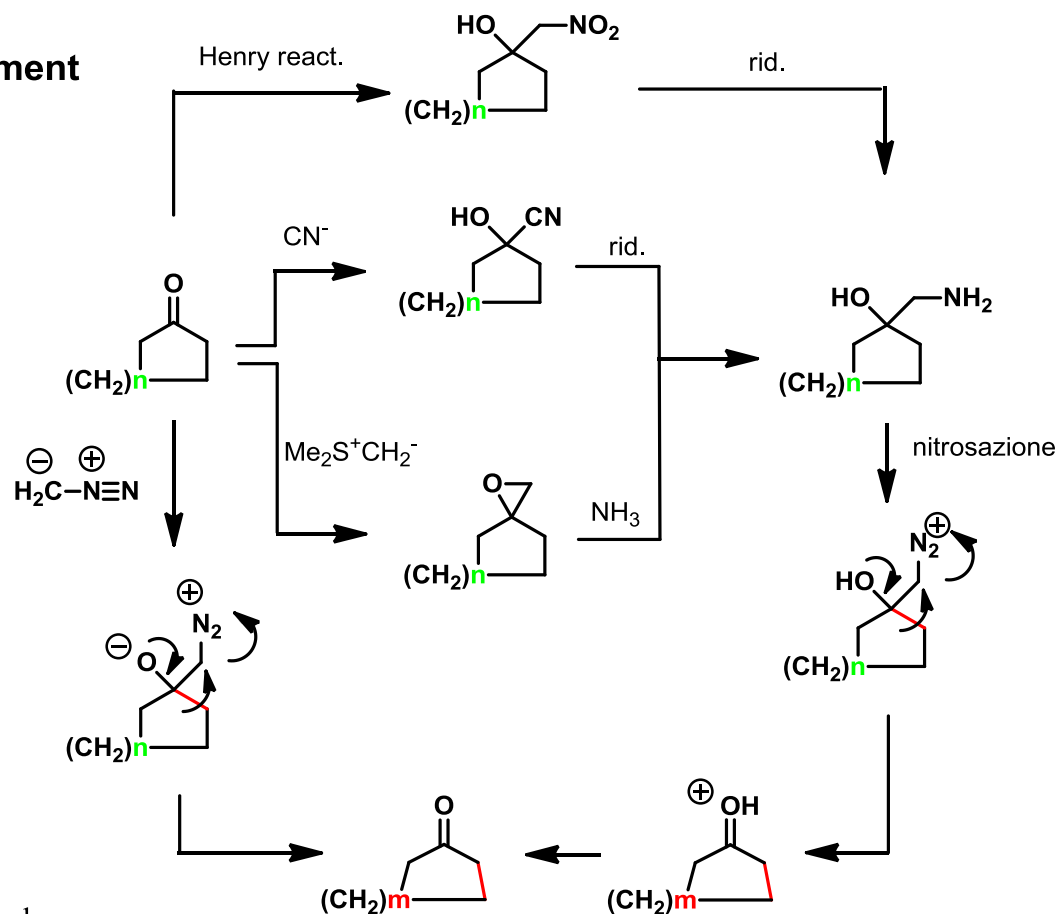


NaNO₂, NaOAc
AcOH, 0°C

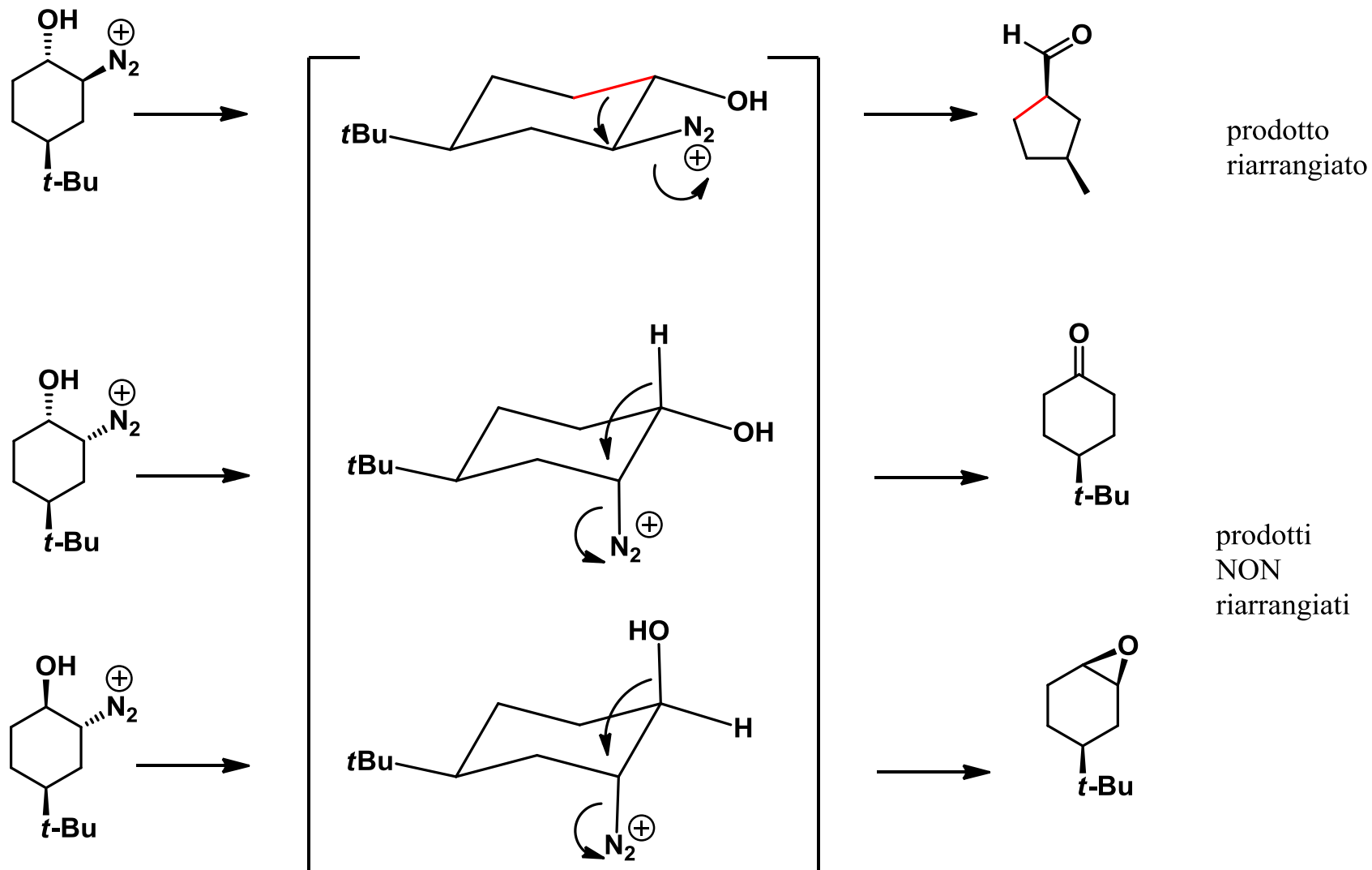


80%

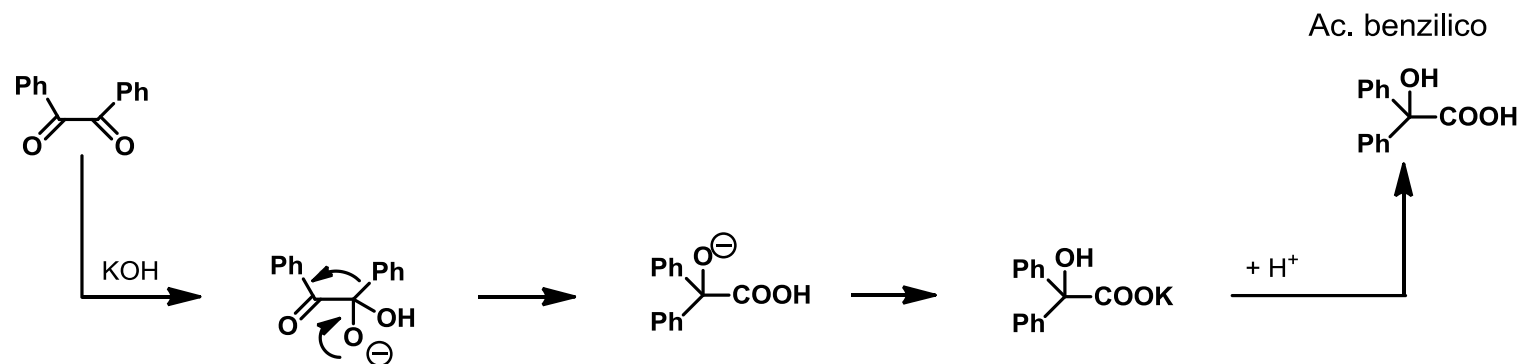
reazione effettuata da R. Woodward
nella sintesi delle PGF₂α



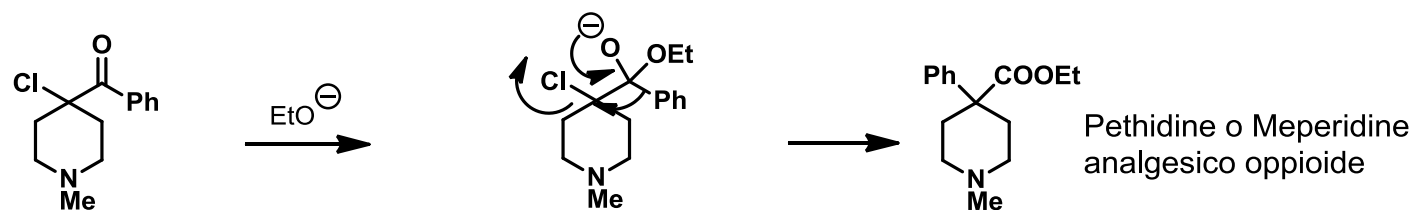
$$m = n + 1$$



riarrangiamento benzilico



α cloro chetone
privo di H in α

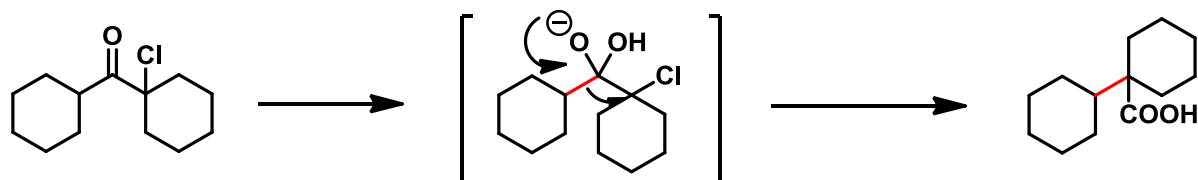


questo riarrangiamento ricorda quello benzilico

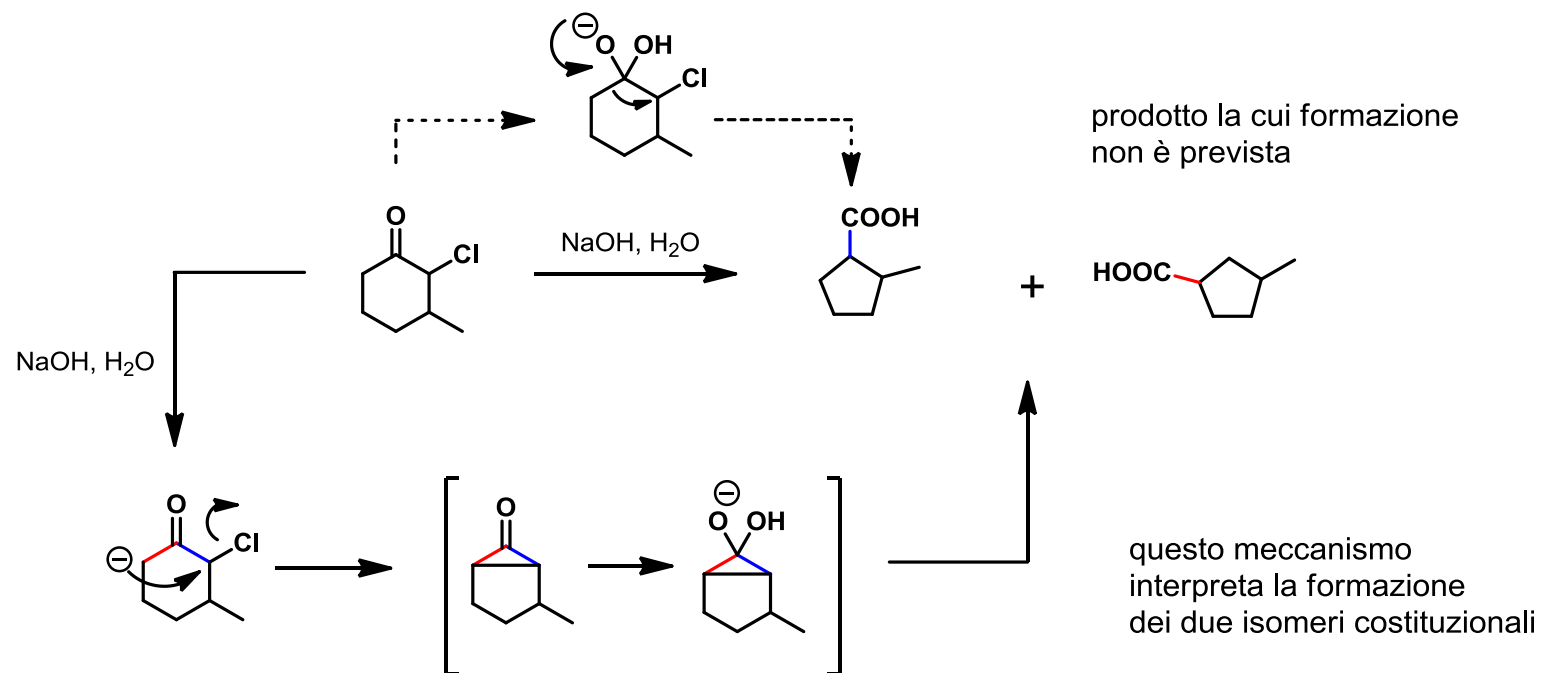
Alexei Yevgrafovich Favorskii
6 March 1860 - 8 August 1945
Russian, b. Pavlovo, Russia

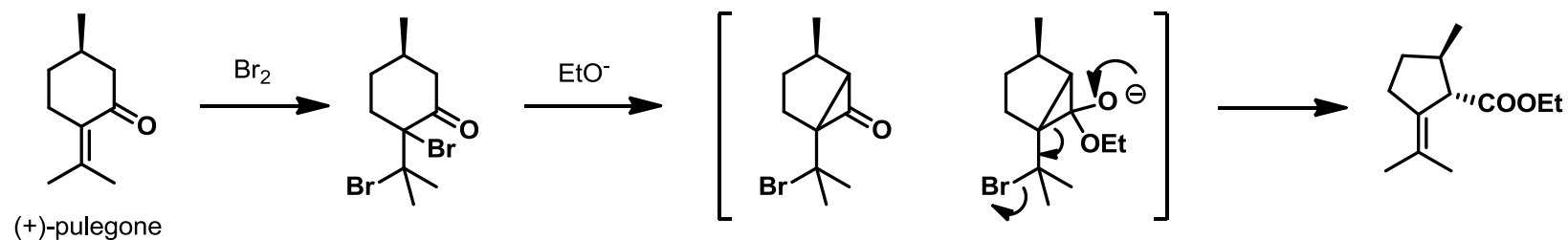
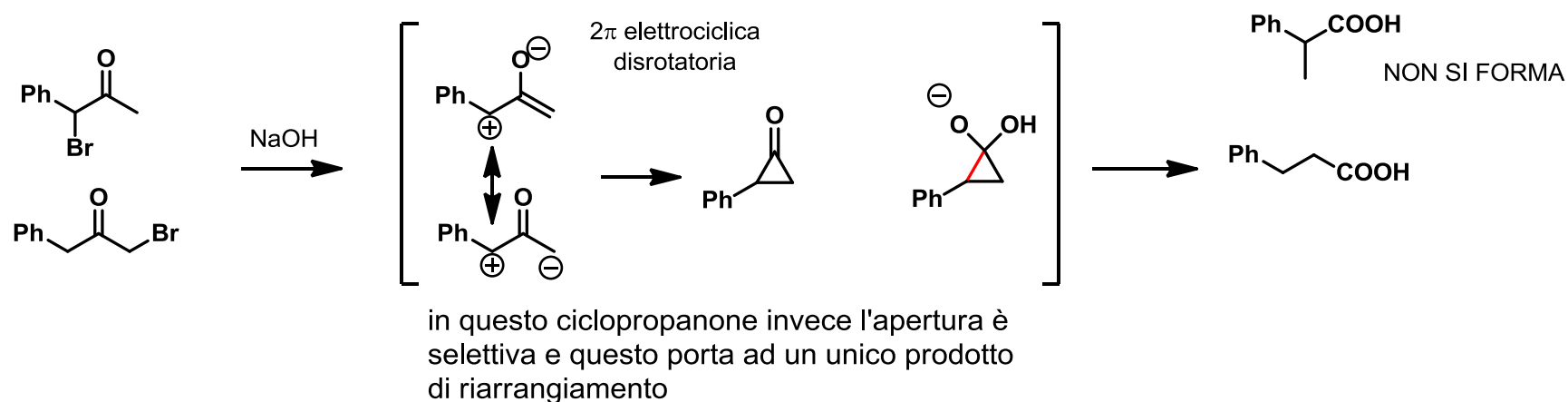
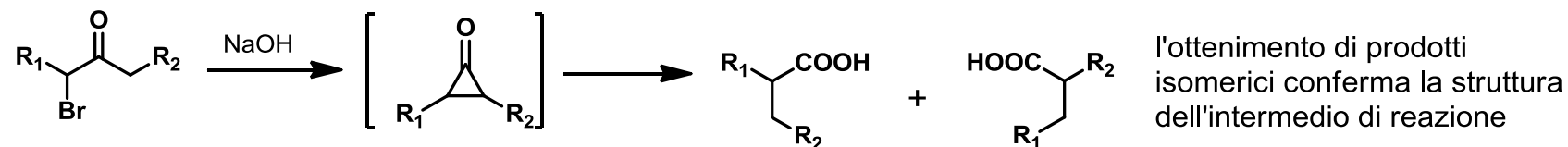
Favorskii rearrangement

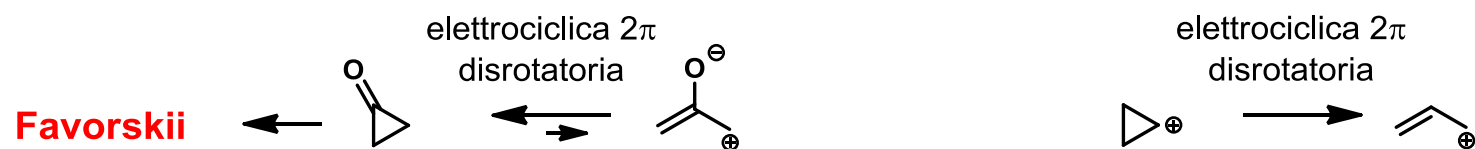
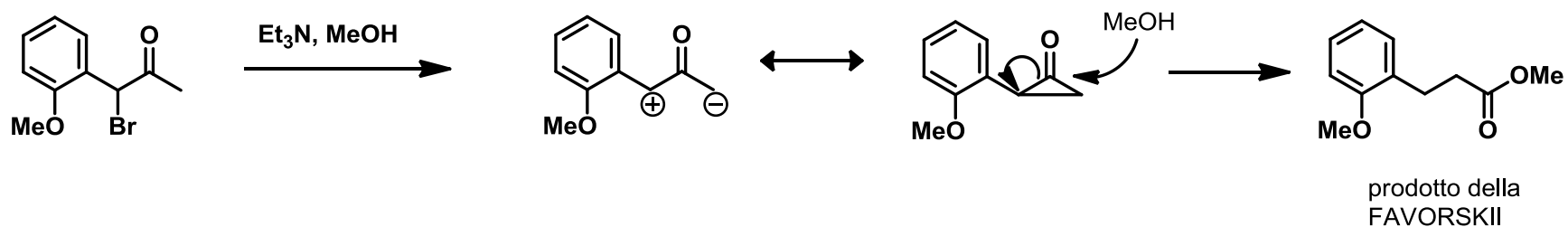
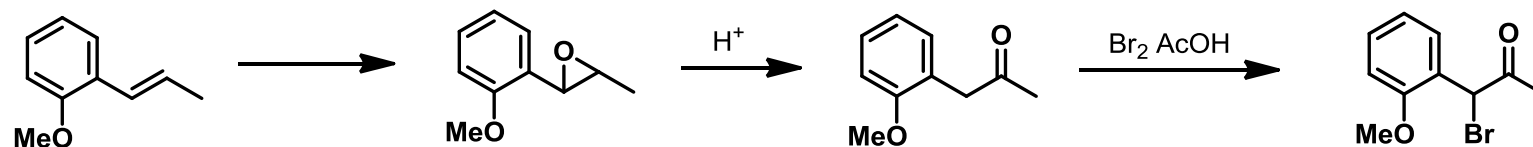
Favorskii, A.E., J. Prakt. Chem. 1913, 88, 658



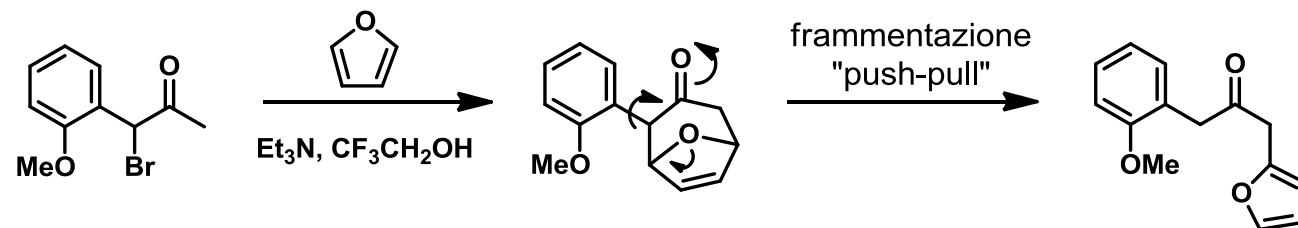
meccanismo accettato fino al 1944, ma...



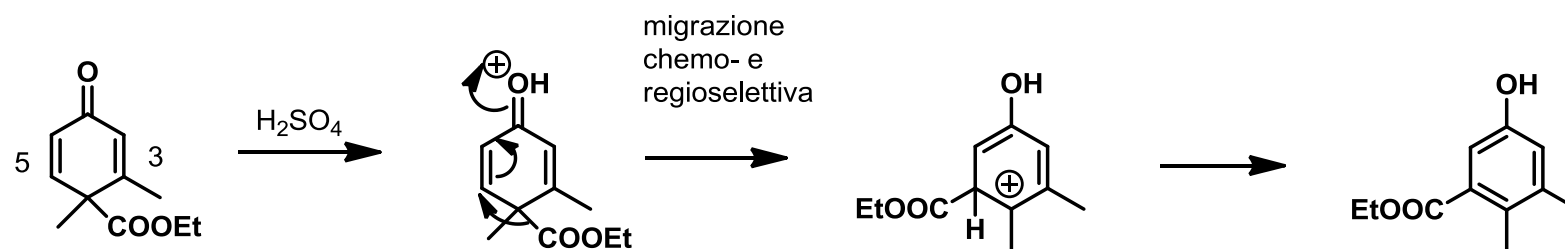




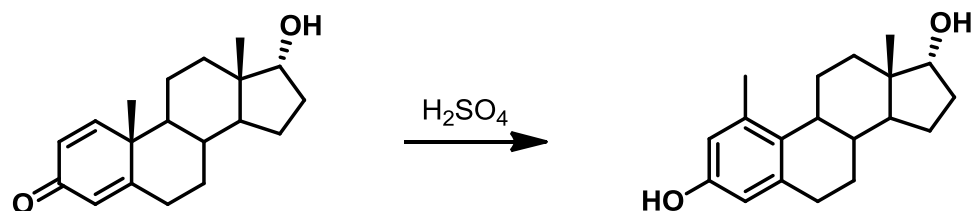
il solvente trifluoroetanolo, poco nucleofilo, rallenta la Favorskii favorendo invece la CICLOADDIZIONE

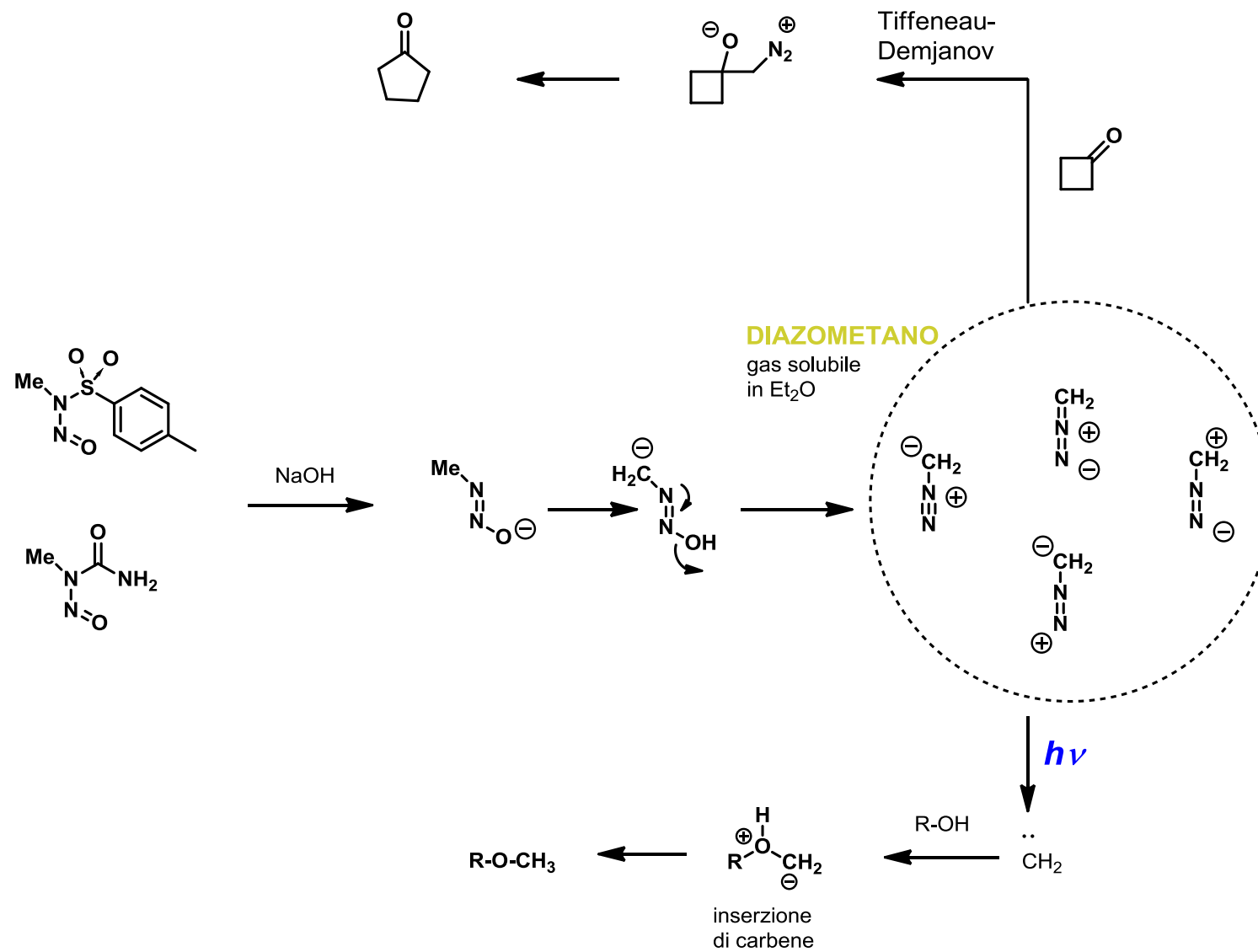


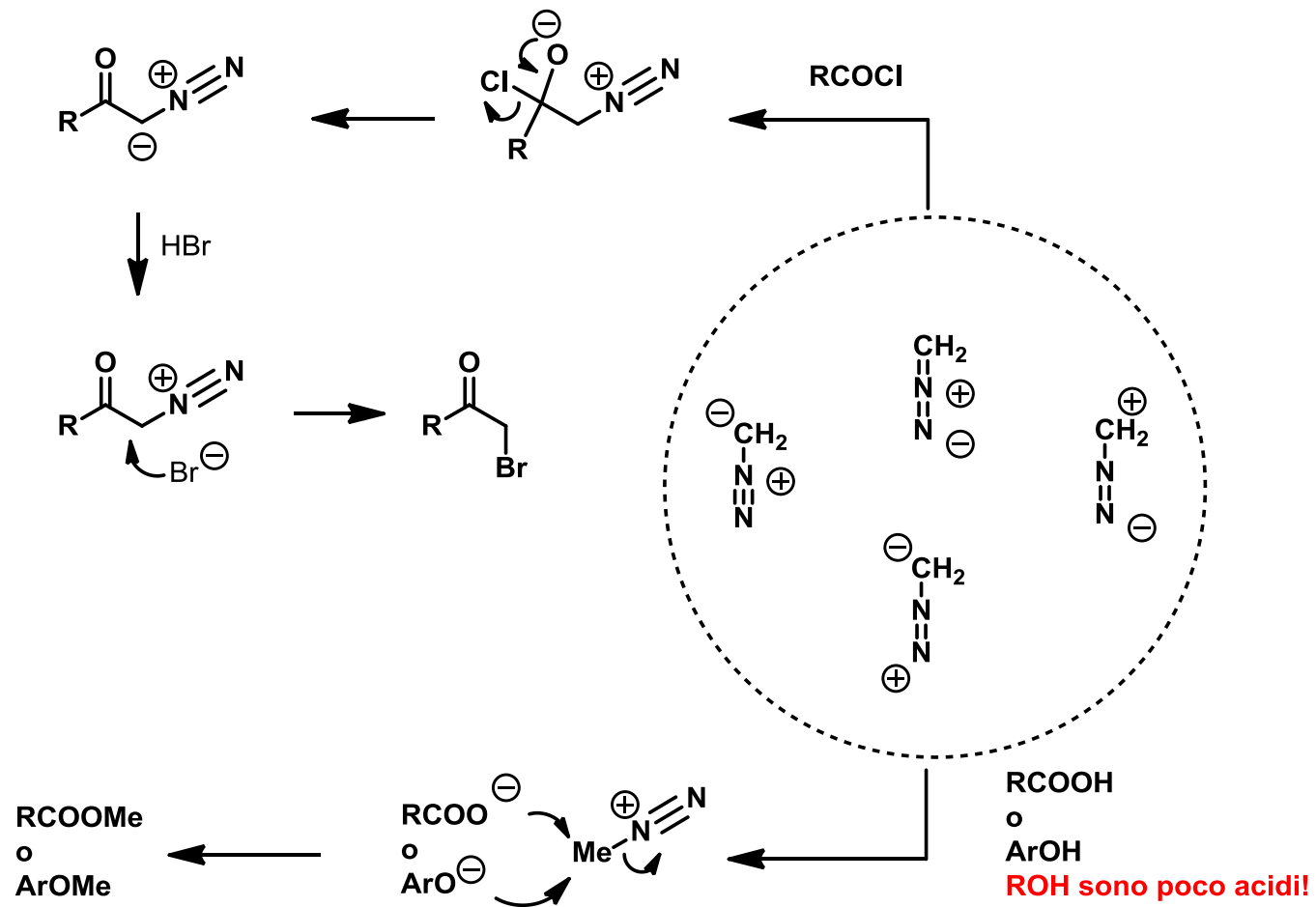
riarrangiamento dienone-fenolo

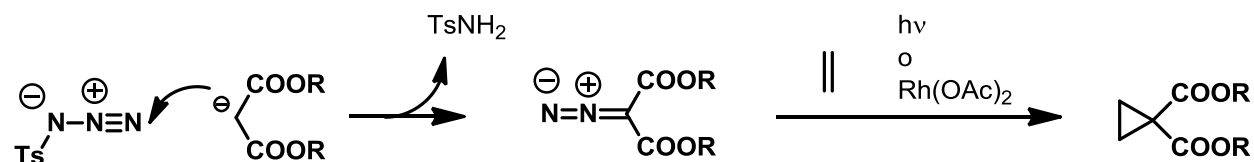


migra il gruppo etossicarbonile e non il metile in modo da ottenere l'intermedio carbocationico più stabile. La migrazione avviene regioselettivamente al C5 stericamente più accessibile del C3. Inoltre la migrazione al C3 non porterebbe ad un prodotto aromatico.

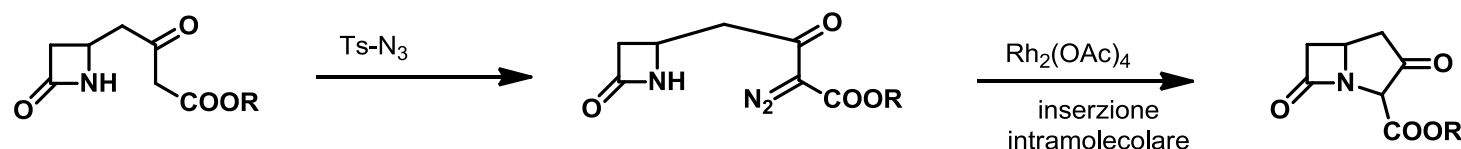




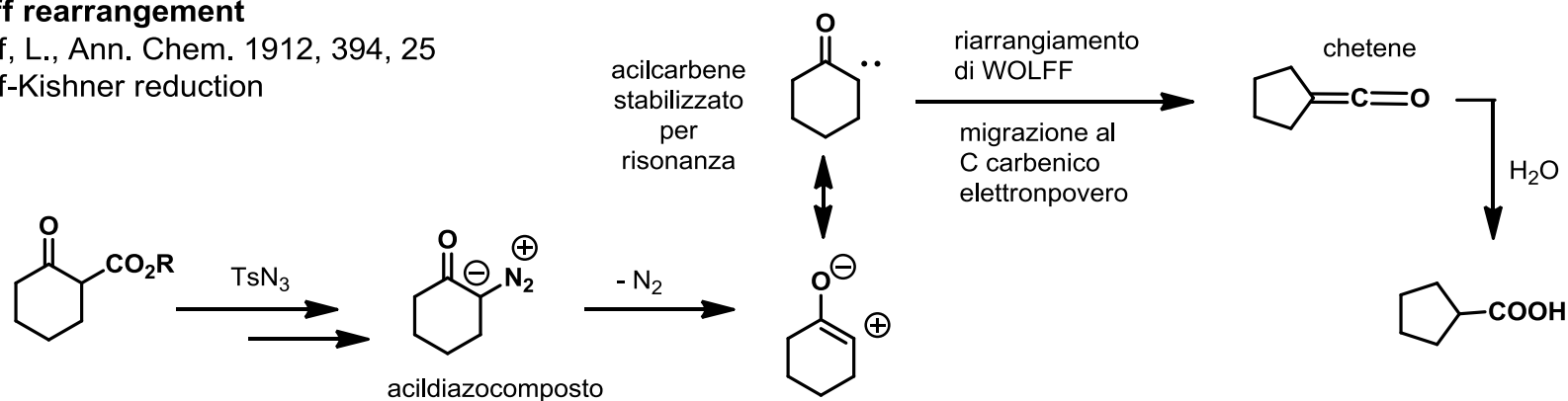


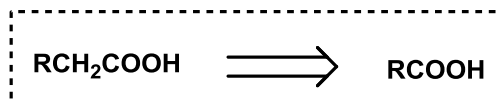


gli acildiazocomposti in presenza di $\text{Rh}_2(\text{OAc})_4$ formano carbenoidi utili in ciclopropanazione di alcheni.
vedi *Simmons-Smith*



Ludwig Wolff
27 September 1857 - 24 February 1919
German, b. Neustadt, Palatinate, Germany
Wolff rearrangement
Wolff, L., Ann. Chem. 1912, 394, 25
Wolff-Kishner reduction





Fritz Arndt

6 July 1885 - 8 December 1969

German, b. Hamburg, Germany

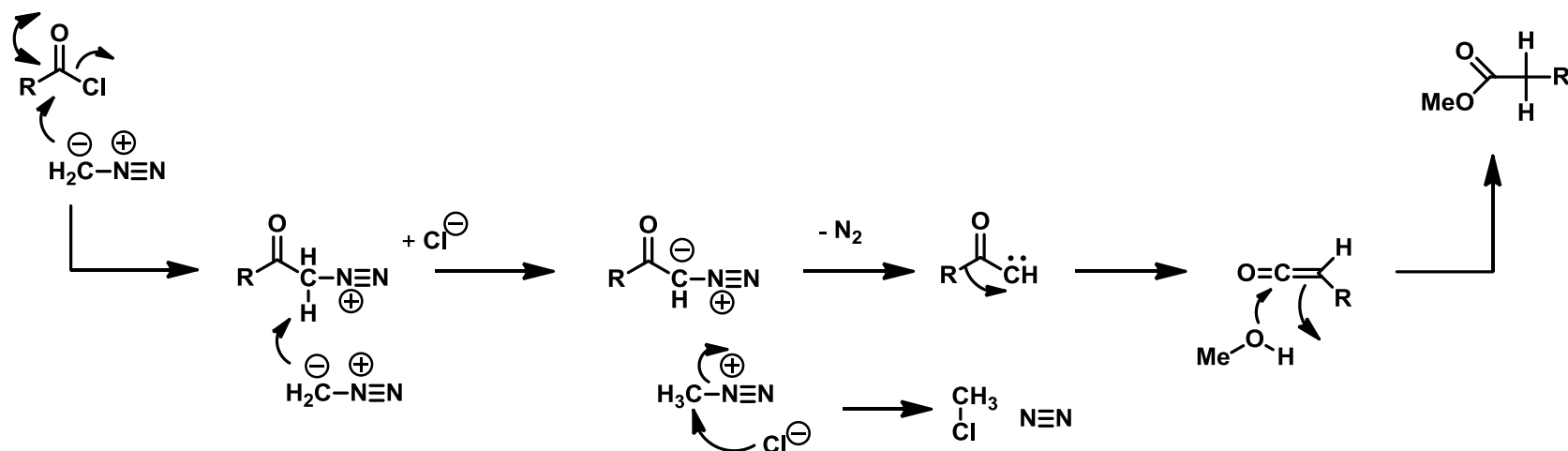
Arndt-Eistert synthesis

Arndt, F.; Eistert, B., Chem. Ber. 1935, 68, 200

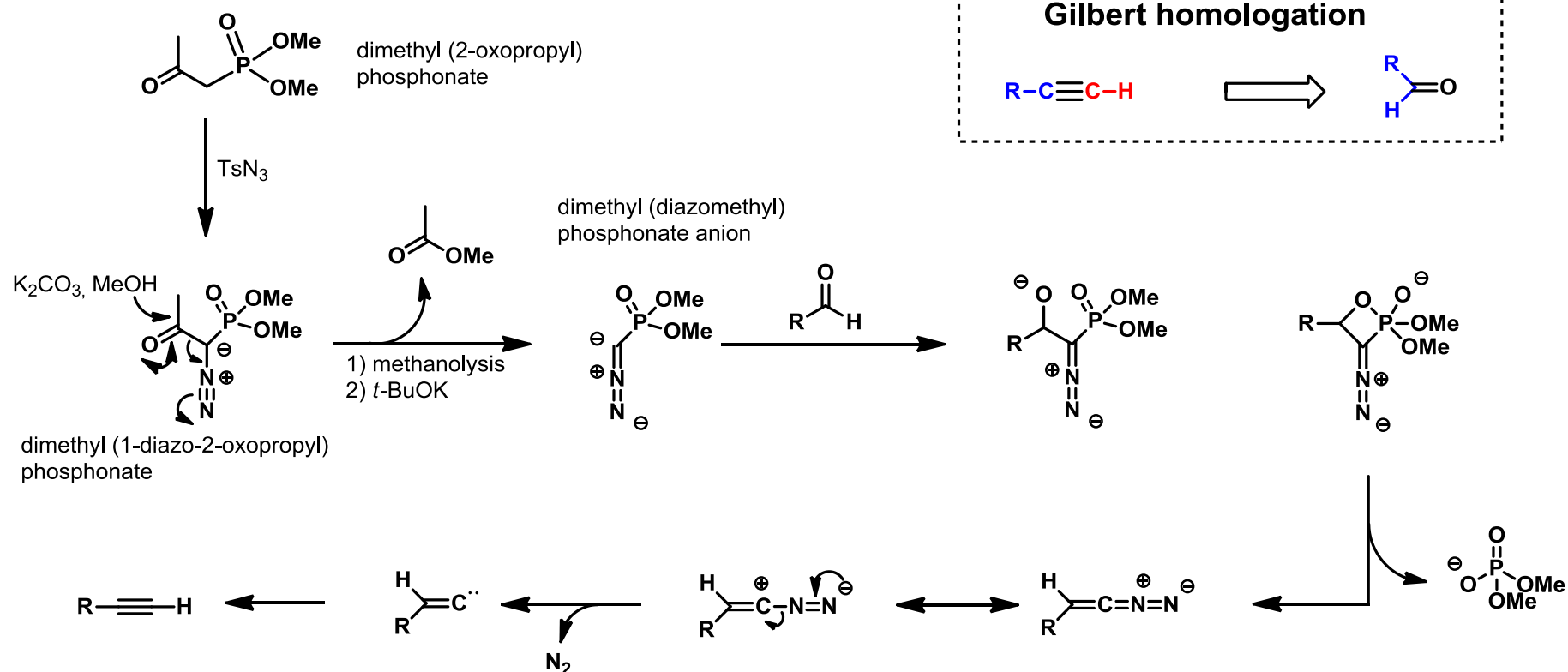
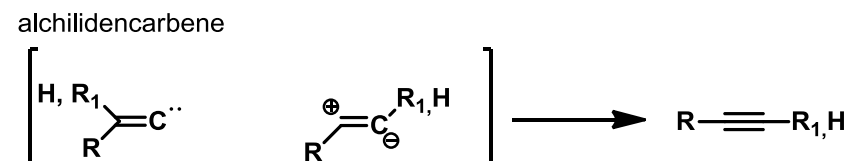
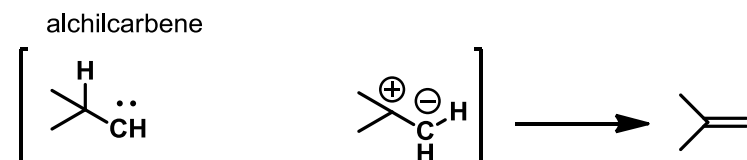
Bernd Eistert

9 November 1902 - 22 May 1978

German, b. Ohlau, lower Silesia, Germany



a differenza degli acil-carbeni, gli alchil- e gli alchiliden-carbeni sono instabili potendo riarrangiare ad alcheni ed alchini rispettivamente.



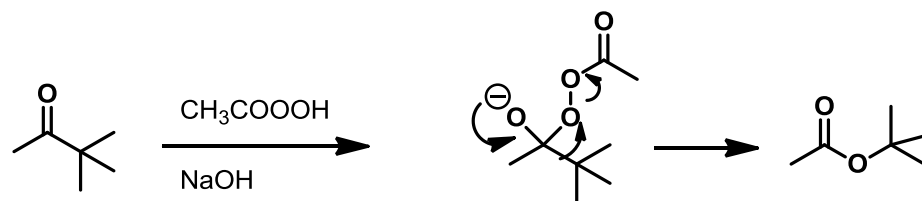
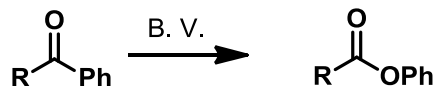
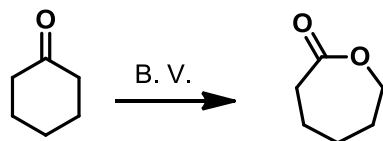
1,2- shift su ossigeno elettronpovero

Johann Friedrich Wilhelm Adolf von Baeyer
31 October 1835 - 20 August 1917
German, b. Berlin, Germany
Nobel Prize Chemistry 1905

Victor Villiger
1 September 1868 - 1934
Swiss, b. Lenzburg, Cham am Zuger See, Aarau, Switzerland

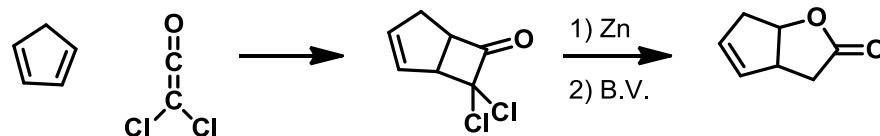
Baeyer-Villiger oxidation

Baeyer, A.; Villiger, V., Chem. Ber. 1899, 32, 3625

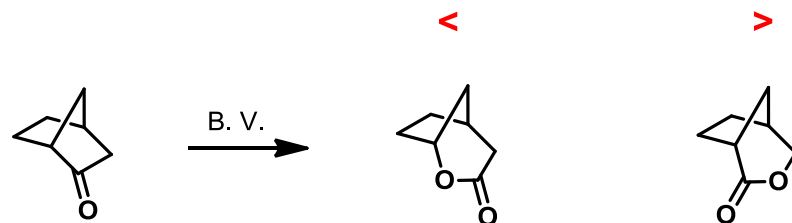


l'inserzione di O è regioselettiva
l'attitudine dei gruppi migranti è:
alchile III > alchile II > benzile > fenile > normal alchile > metile
TS cationico

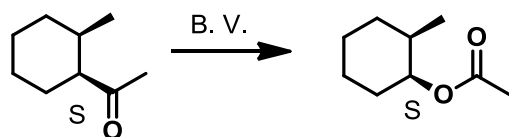
andamento opposto si osserva nell'ossidazione
dei borani a borati.
TS anionico



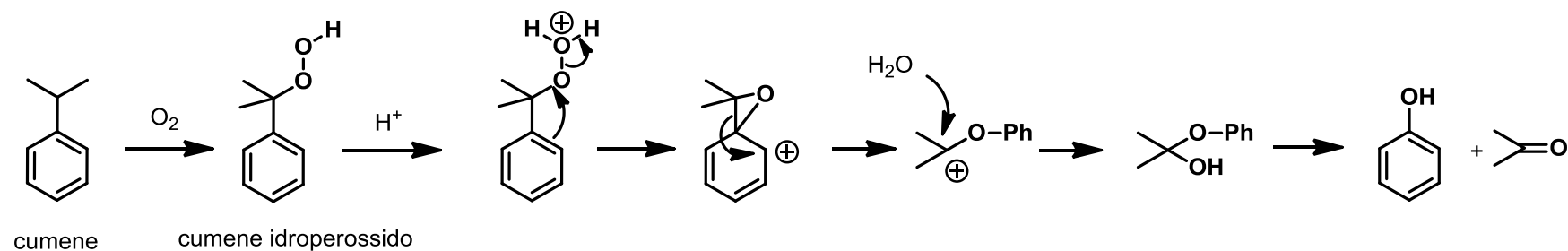
1,2- shift su ossigeno elettronpovero



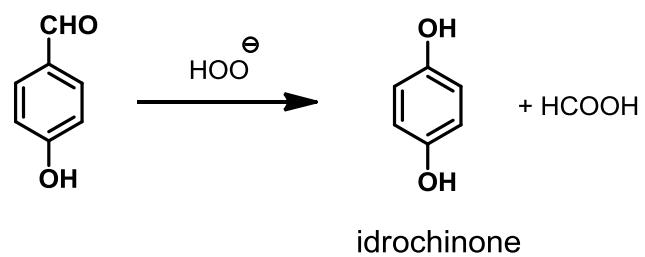
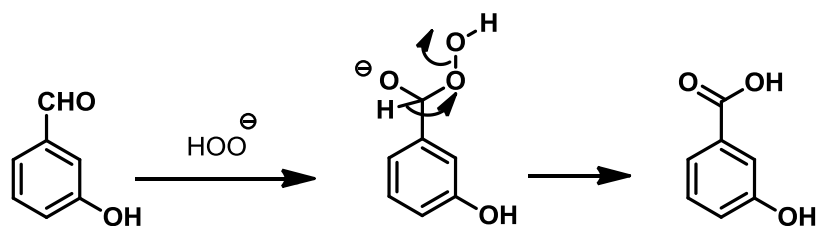
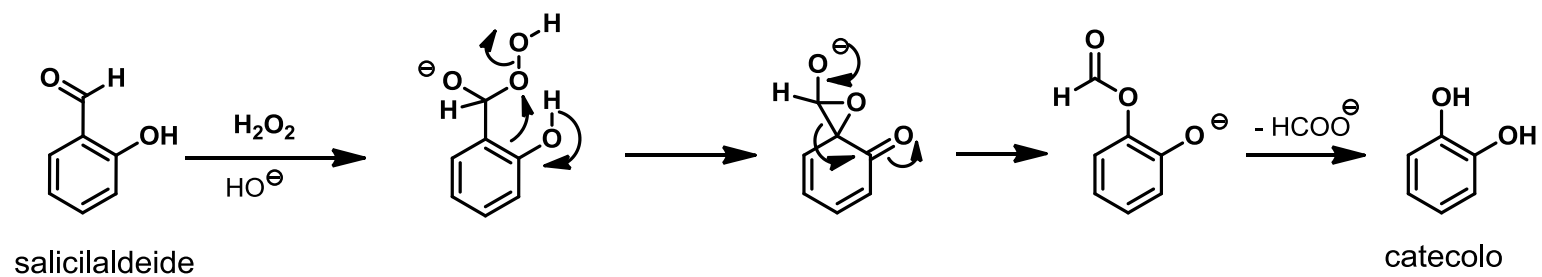
la testa di ponte fatica a migrare



reazione regioselettiva
e
stereospecifica: il gruppo migrante conserva la configurazione



reazione di
Dakin



1,2 shift su azoto elettronpovero

August Wilhelm von Hofmann

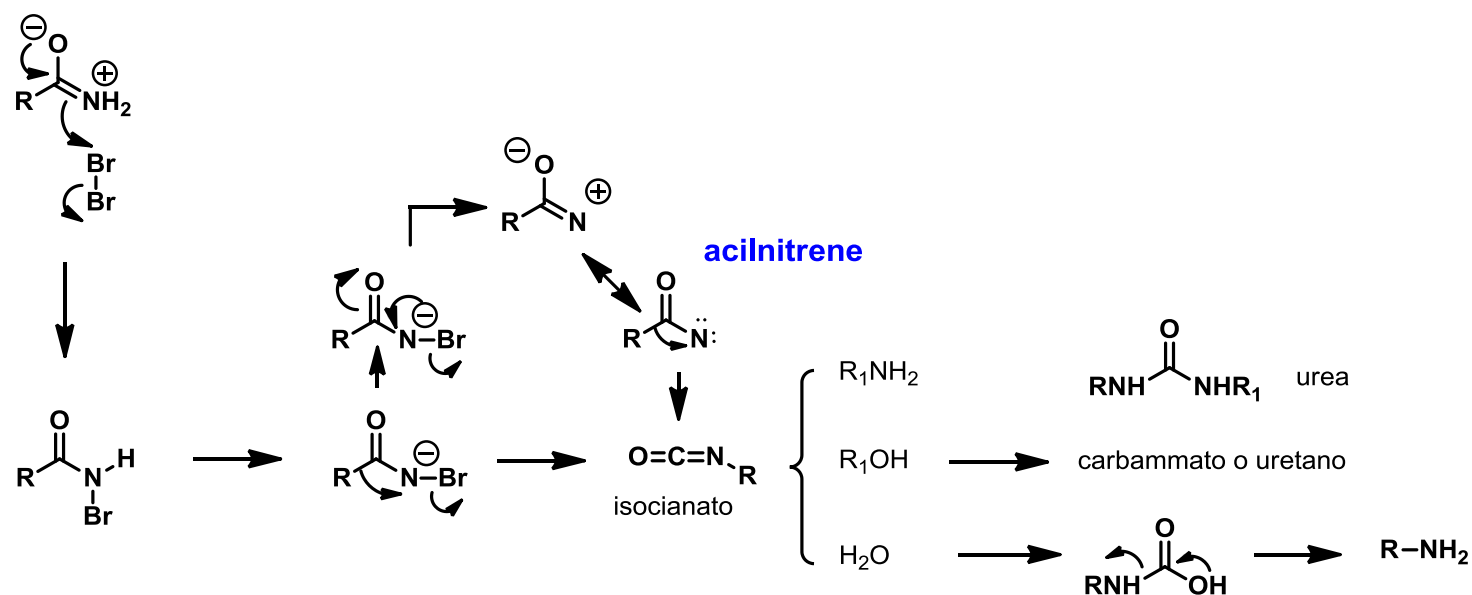
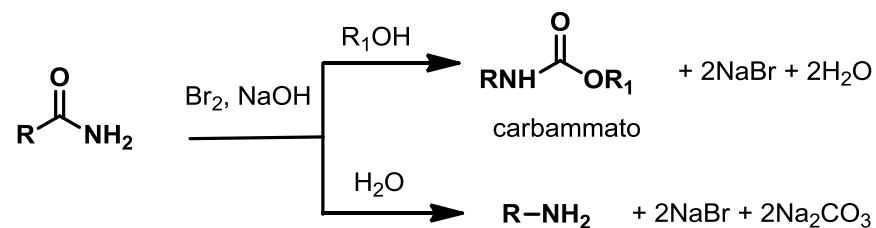
8 April 1818 - 2 May 1892

German, b. Giessen, Germany

Hofmann degradation (elimination)

Hofmann, A.W., Chem. Ber. 1881, 14, 659

Hofmann-



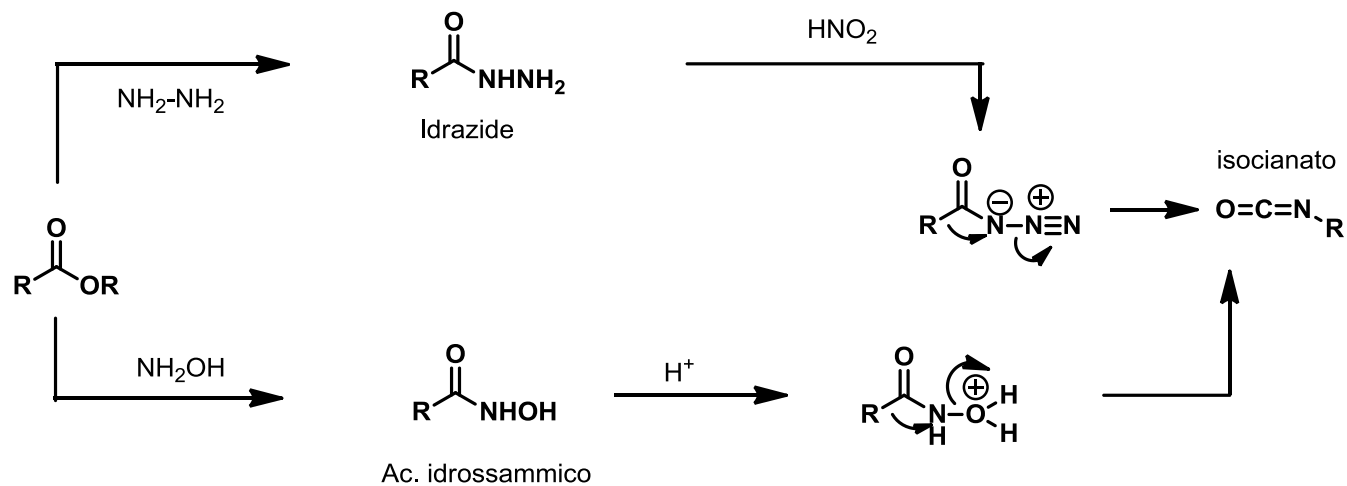
Theodor Curtius

27 May 1857 - 8 February 1928

German, b. Duisburg, Ruhr, Germany

Curtius rearrangement

Curtius, T., Chem. Ber. 1890, 23, 3023



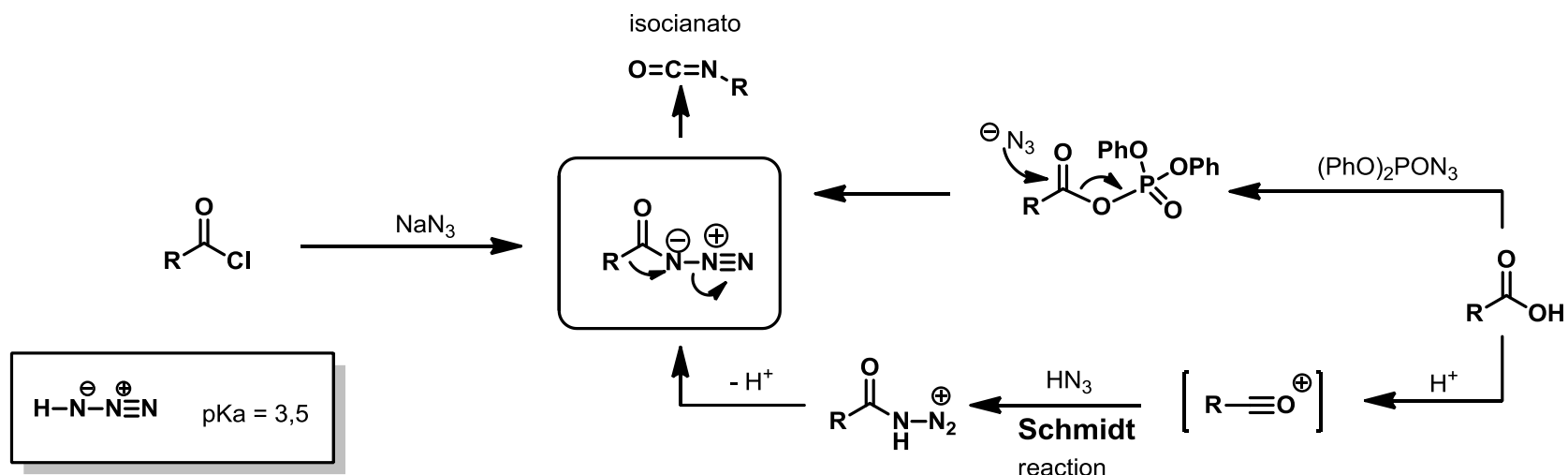
Wilhelm Lossen

8 May 1838 - 29 October 1906

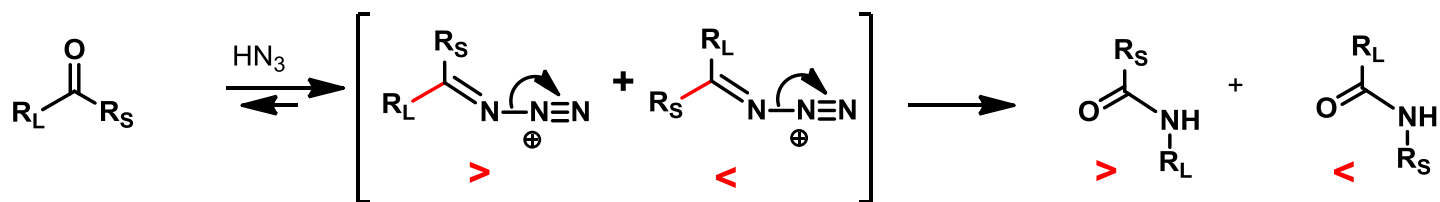
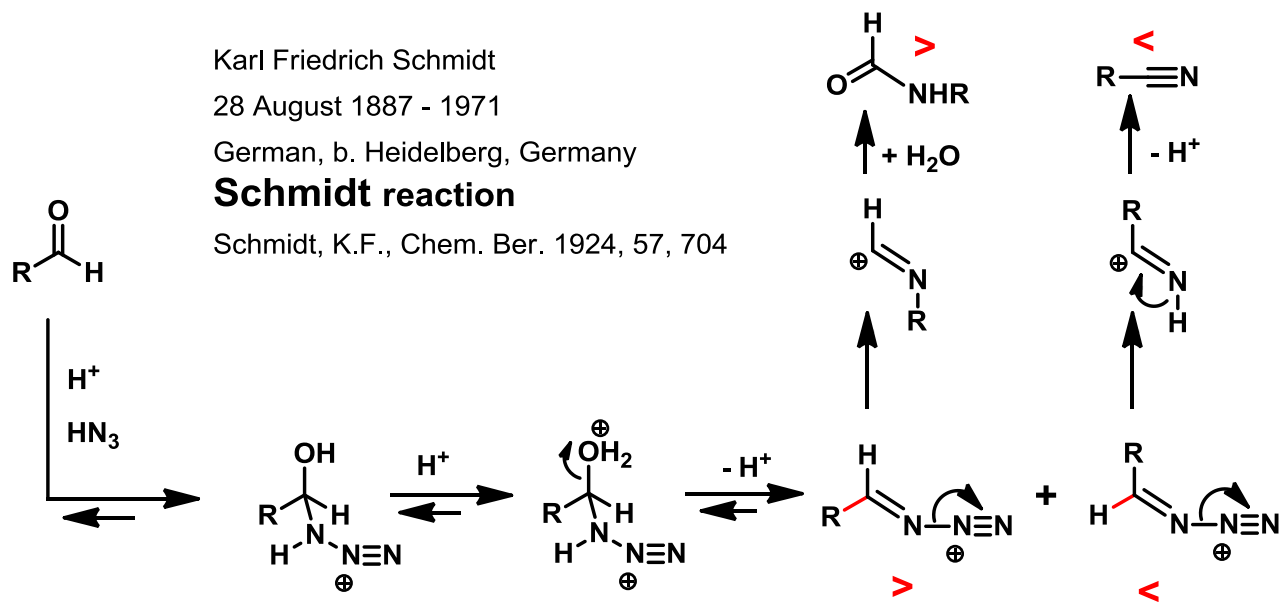
German, b. Kreuznach, Germany

Lossen rearrangement

Lossen, W., Ann. Chem. 1872, 161, 347

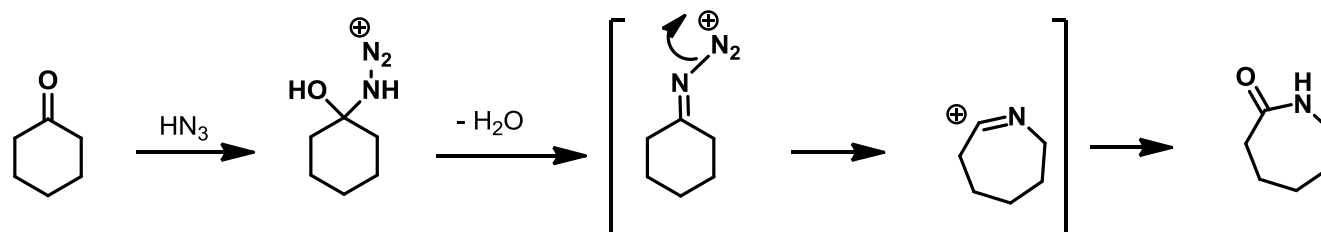
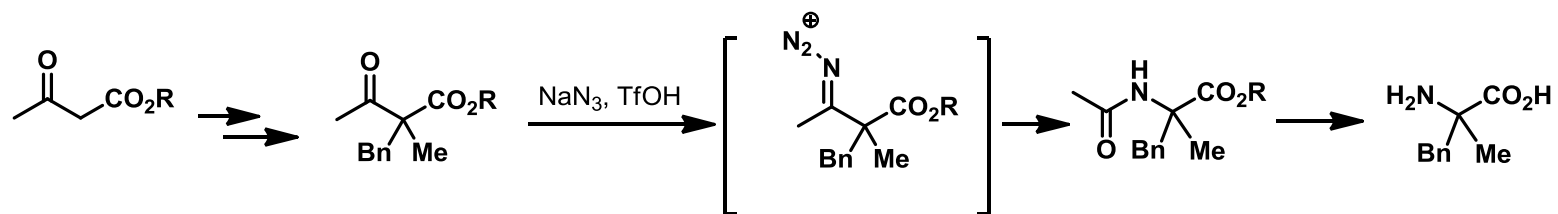


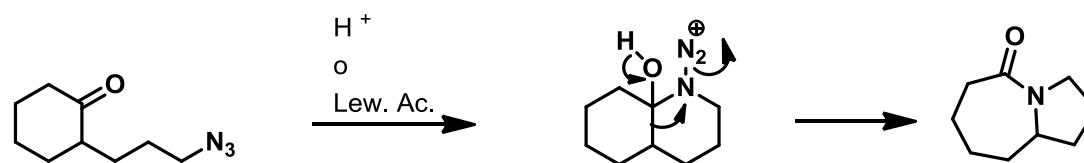
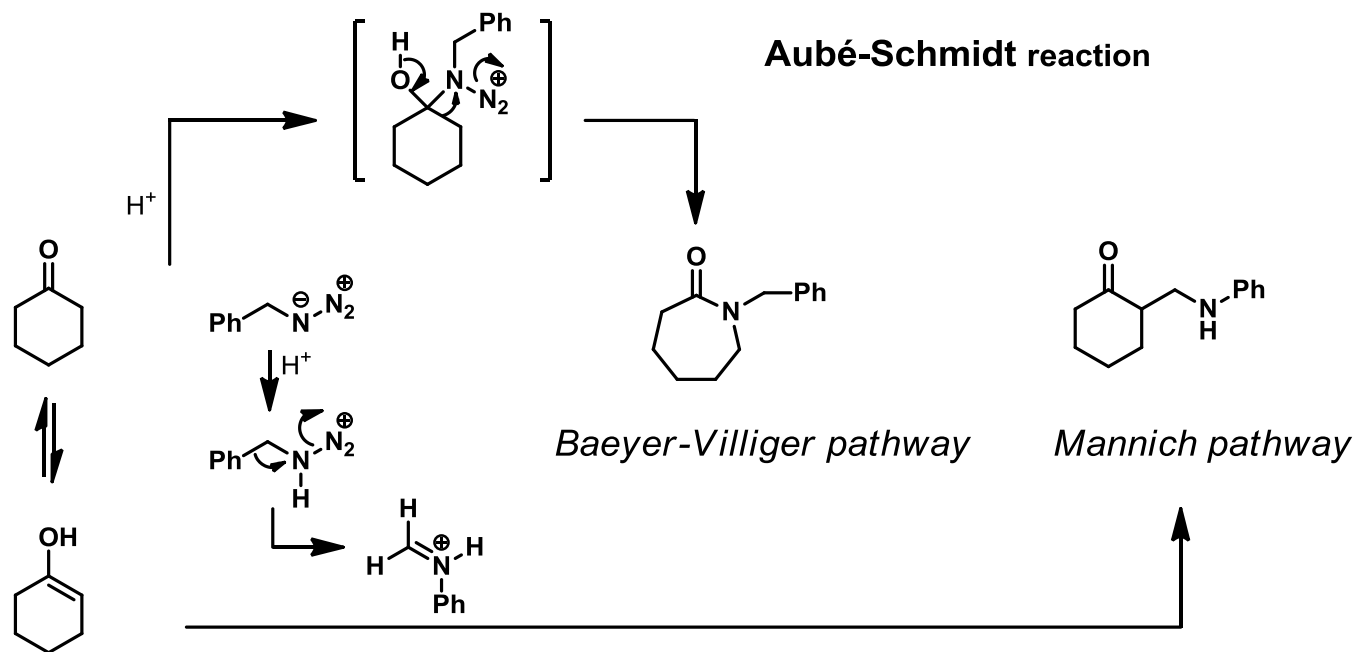
Karl Friedrich Schmidt
 28 August 1887 - 1971
 German, b. Heidelberg, Germany
Schmidt reaction
 Schmidt, K.F., Chem. Ber. 1924, 57, 704



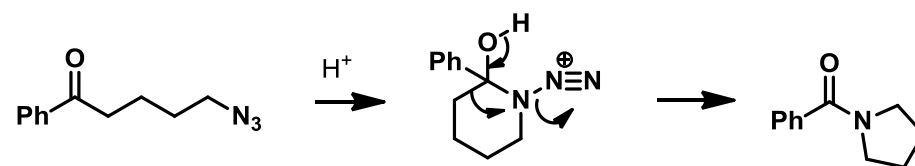
Beckmann pathway

Beckmann pathway

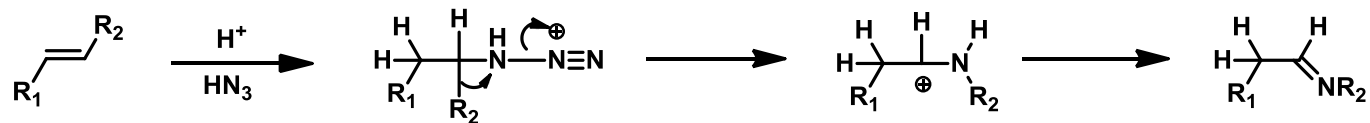
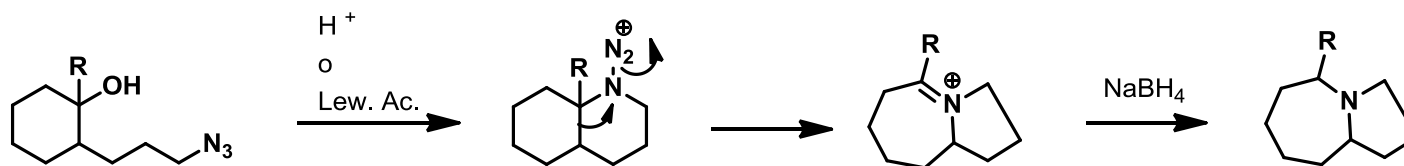




Baeyer-Villiger pathways



Pearson-Schmidt reactions



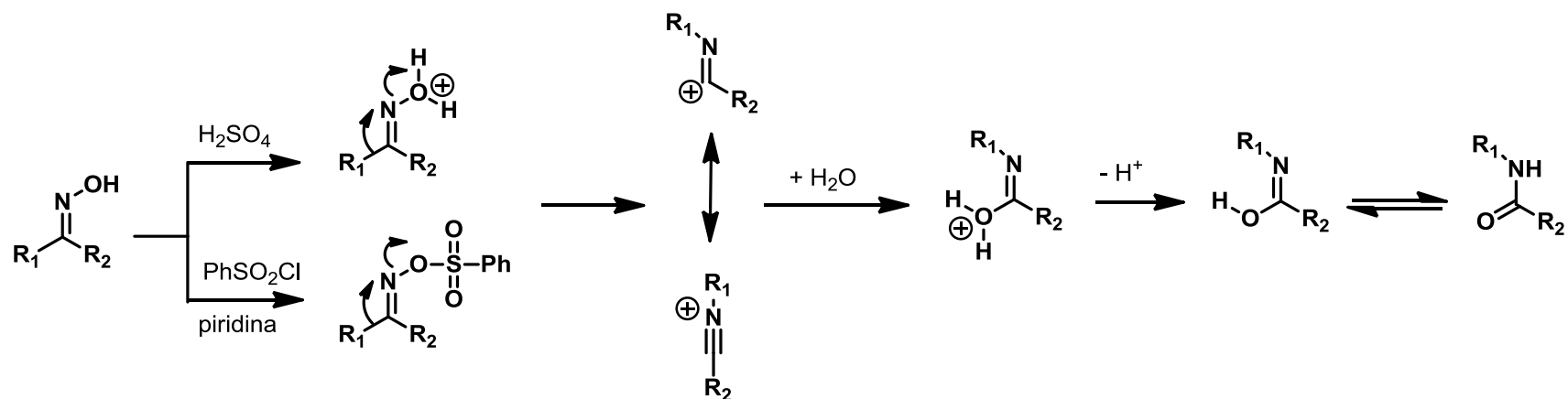
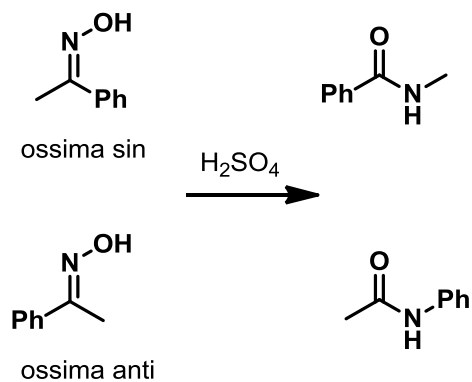
Ernst Otto Beckmann

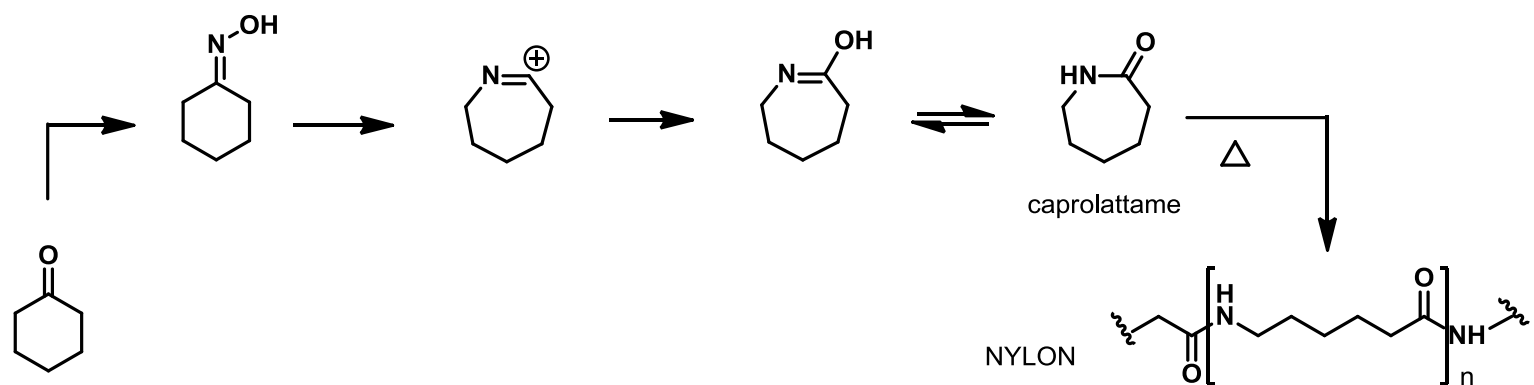
4 July 1853 - 12 July 1923

German, b. Sölingen, Germany

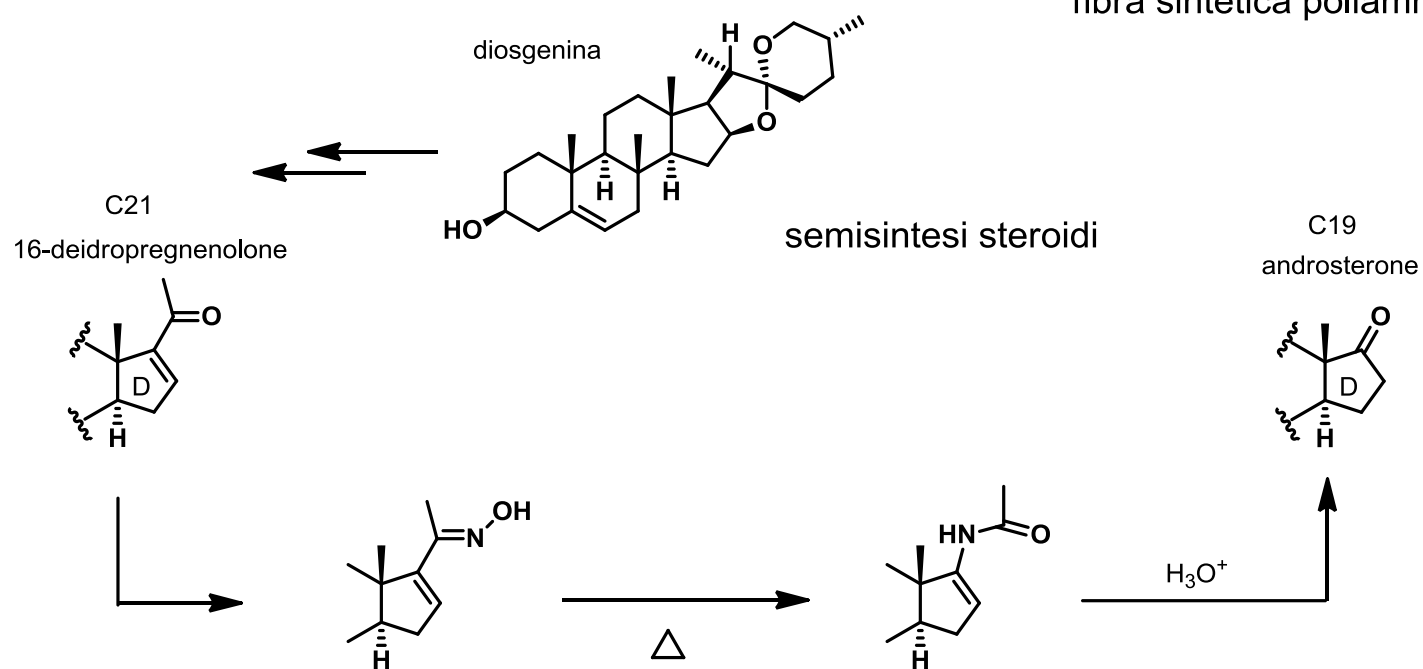
Beckmann rearrangement

Beckmann, E., Chem. Ber. 1886, 19, 988

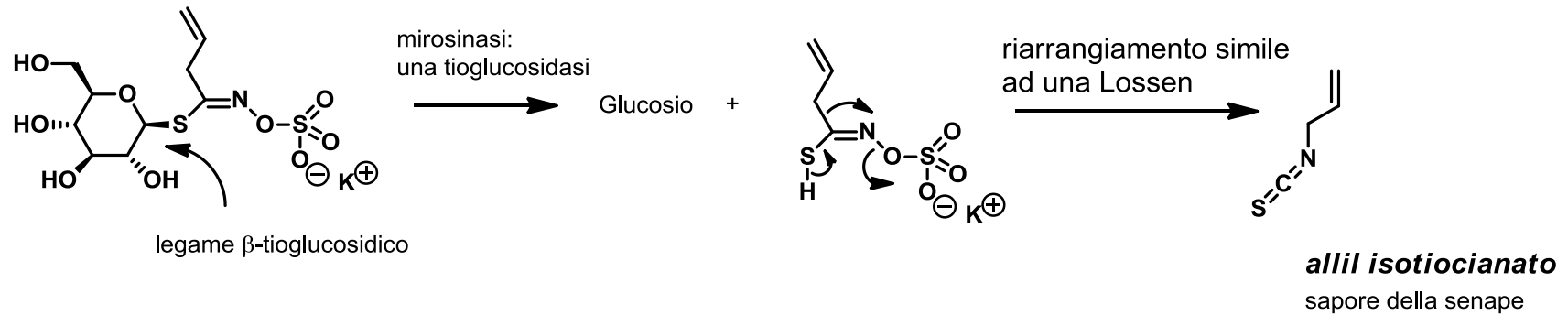




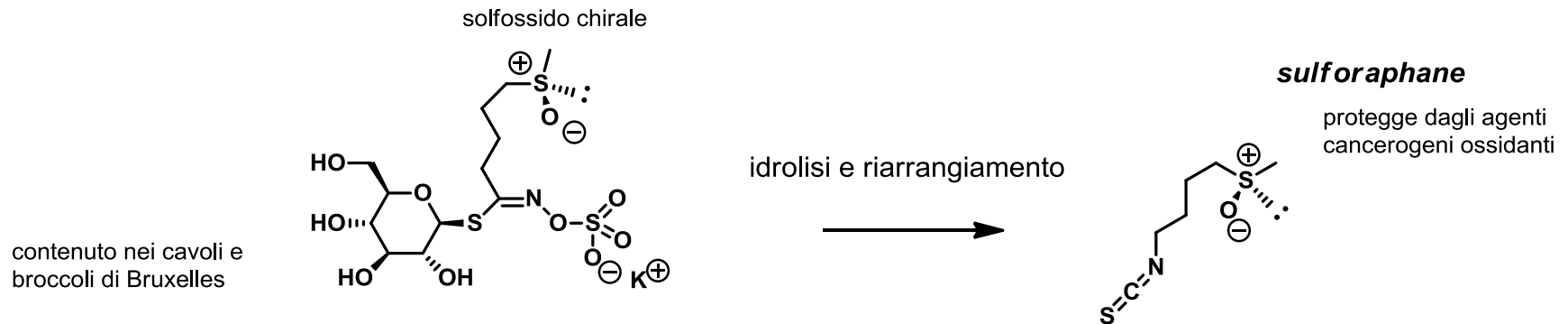
fibra sintetica poliammidica



sinigrina: un glucosinolato del rafano, cren e senape



meccanismo di difesa chimica delle piante



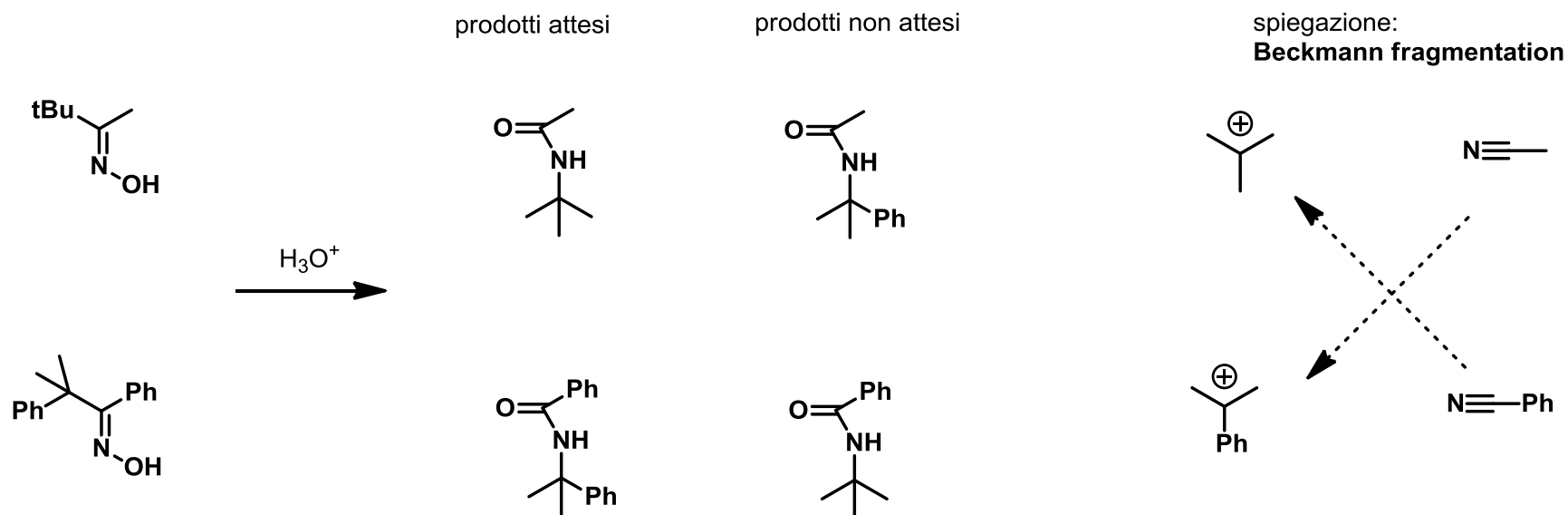
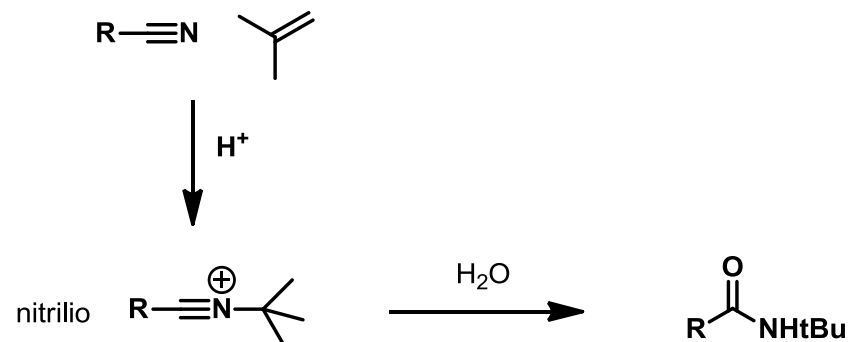
John Joseph Ritter

25 July 1895 - ?

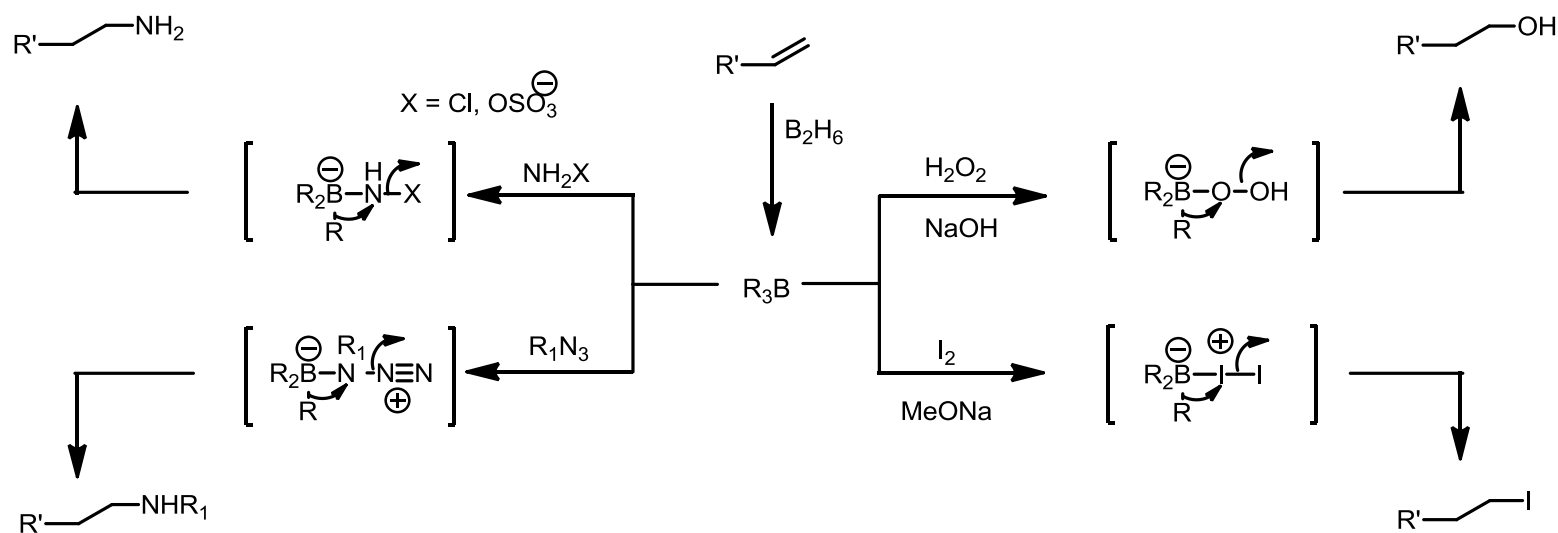
American, b. New York, New York, USA

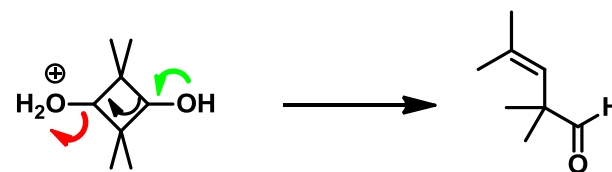
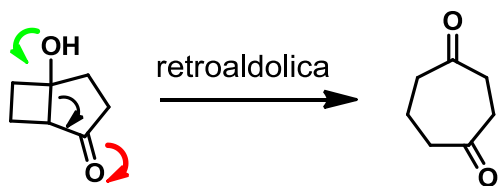
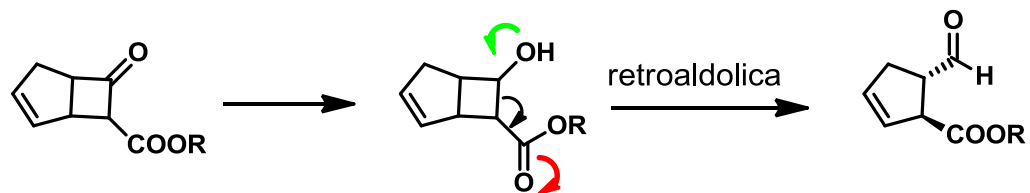
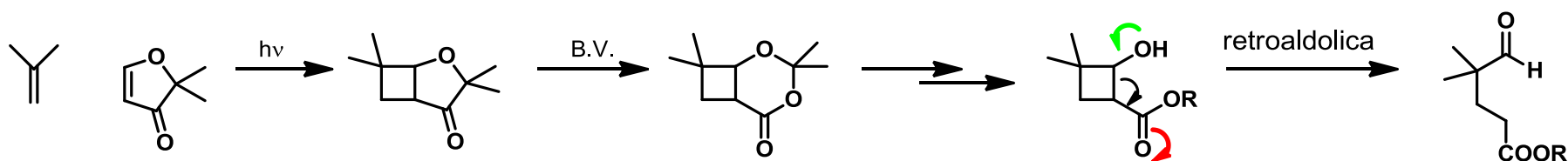
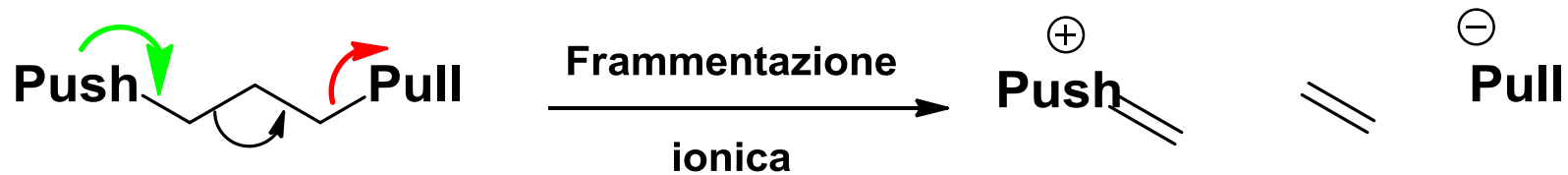
Ritter reaction

Ritter, J.J.; Minieri, P.P., J. Am. Chem. Soc. 1948, 70, 4045

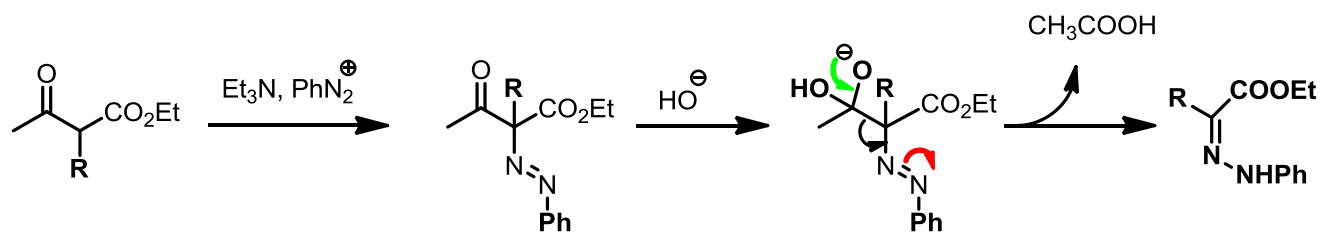
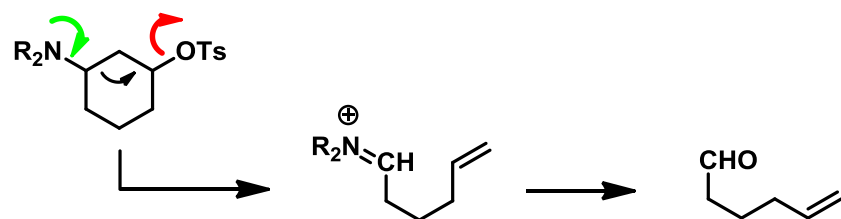
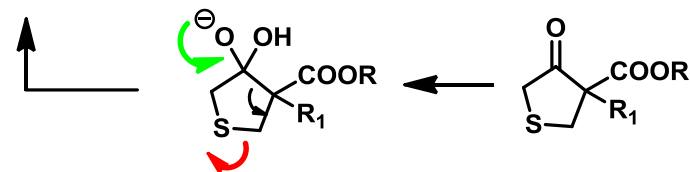
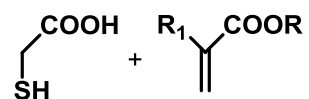
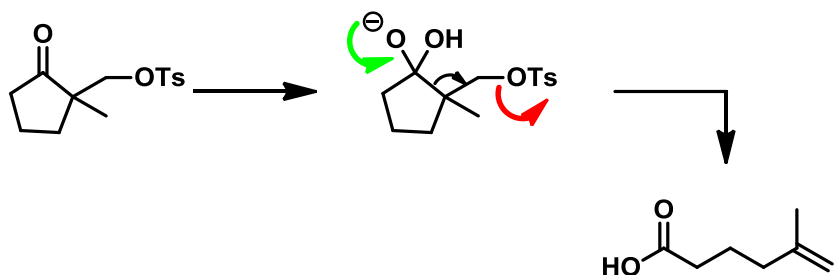


Riarrangiamenti da B(ate complex) ad O, I, N elettronpoveri





accomuna questo gruppo di frammentazioni ioniche l'apertura del tensionato anello a 4 termini



Albert Eschenmoser

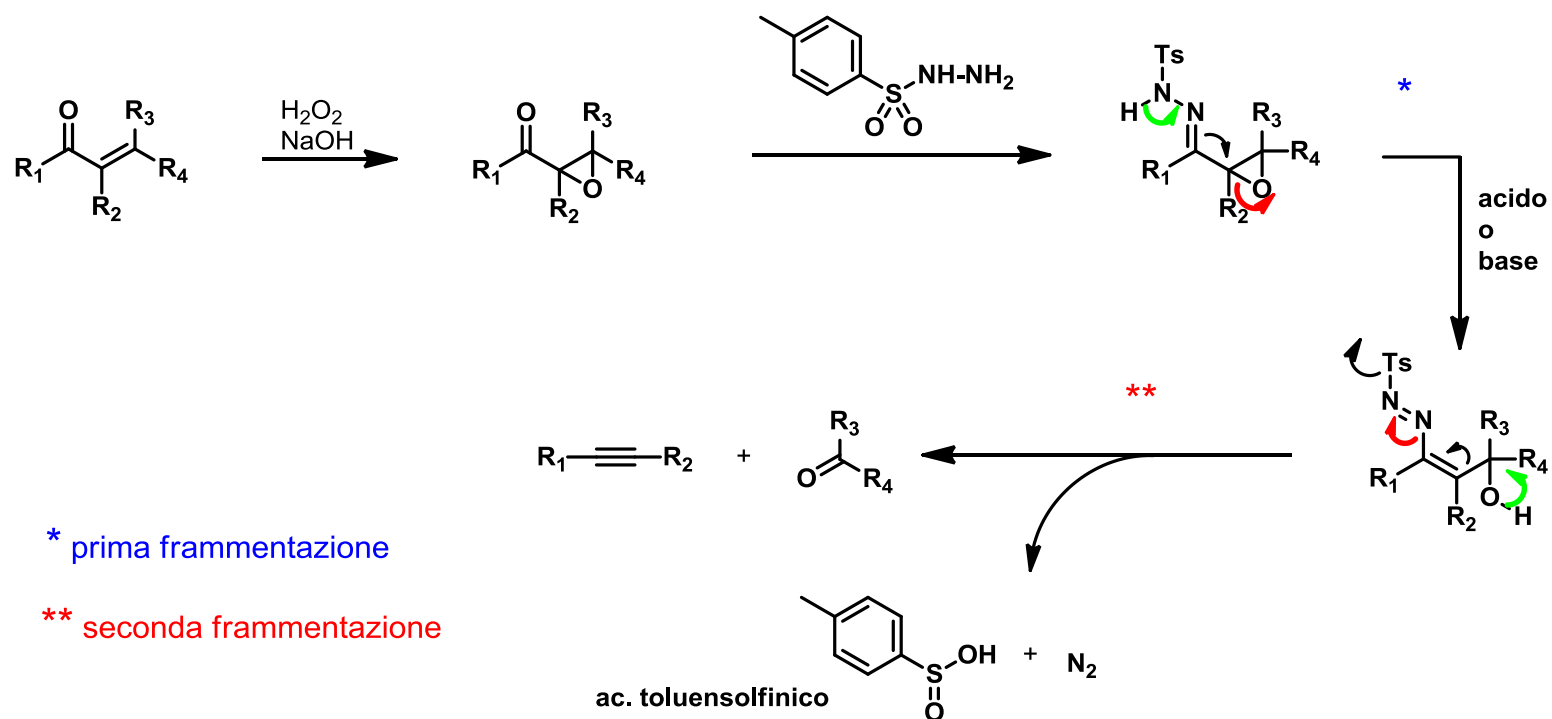
5 August 1925 -

Swiss, b. Erstfeld, Switzerland

Dr. John Andraos, [http://www.careerchem.com/NAMED/Named-Rxns\(E-H\).pdf](http://www.careerchem.com/NAMED/Named-Rxns(E-H).pdf) 4

Eschenmoser fragmentation

Eschenmoser, A.; Felix, D.; Ohloff, G. *Helv. Chim. Acta* 1967, 50, 708

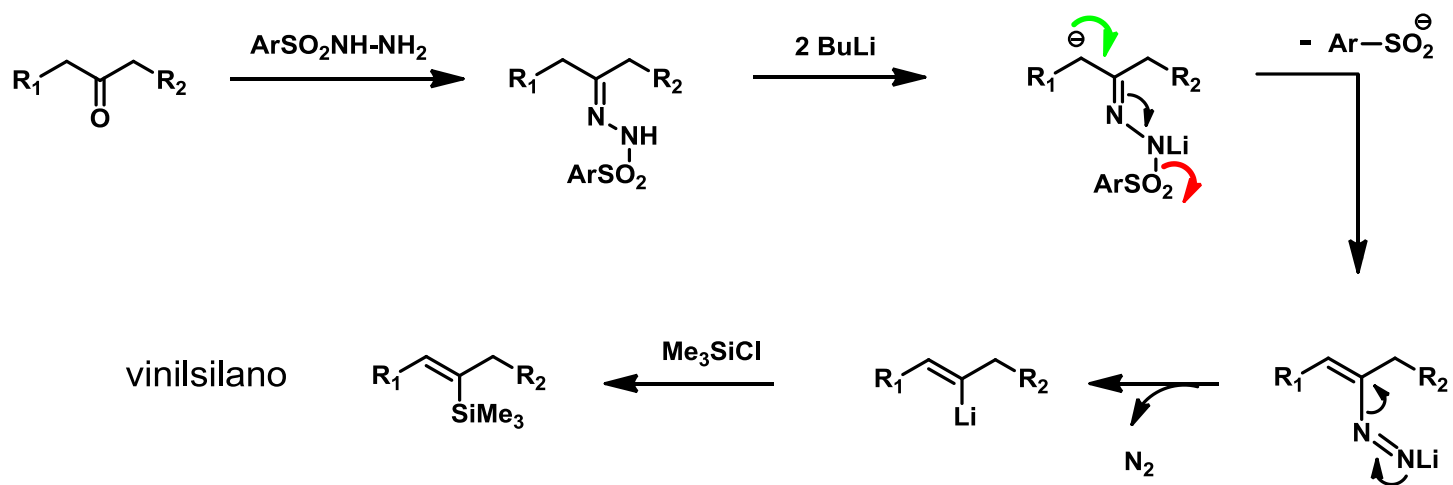


* prima frammentazione

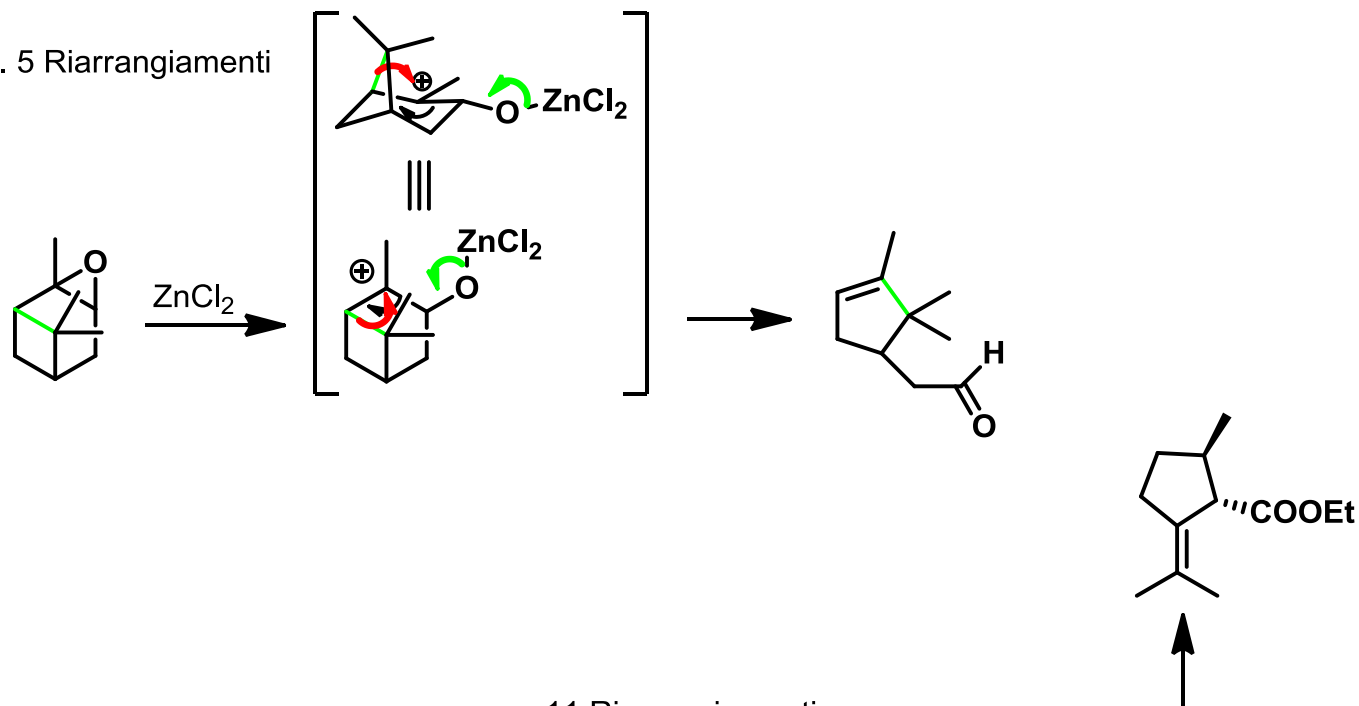
** seconda frammentazione



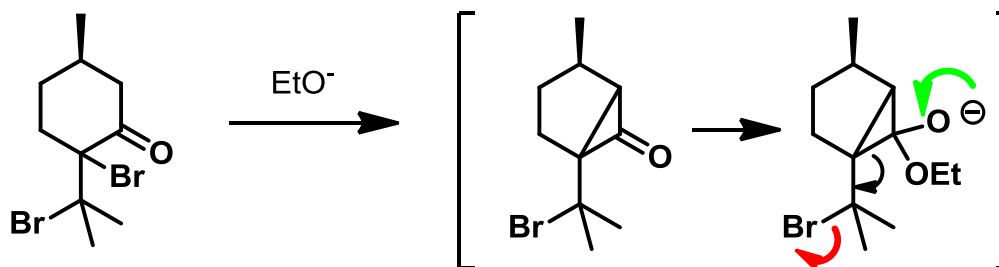
Shapiro reaction

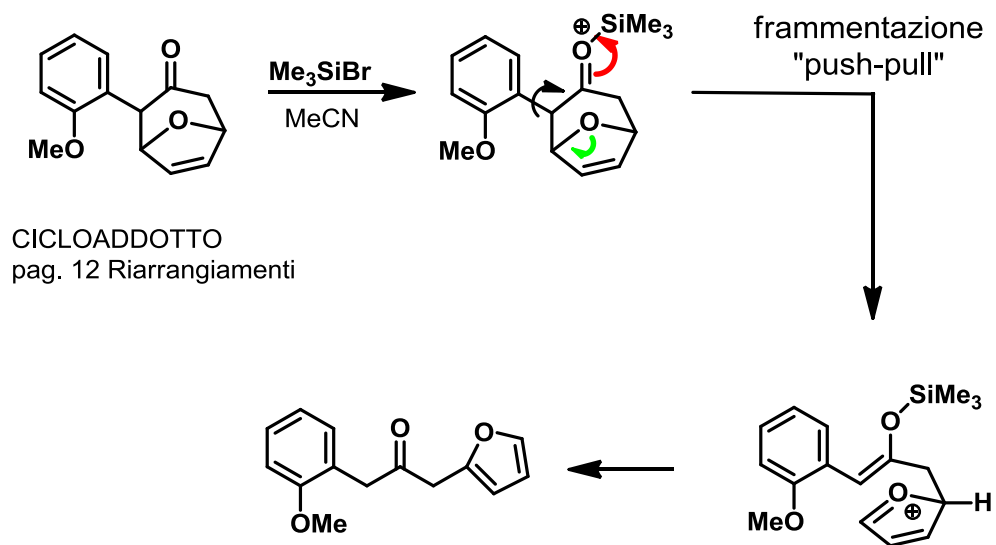


pag. 5 Riarrangiamenti



pag. 11 Riarrangiamenti





CICLOADDOTTO
pag. 12 Riarrangiamenti

