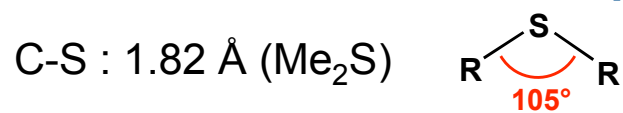
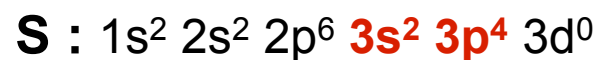
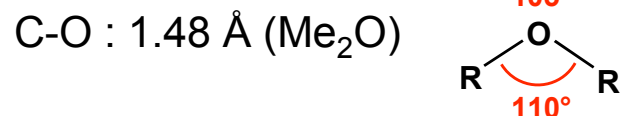


2 Soufre

□ 2.1 Généralités

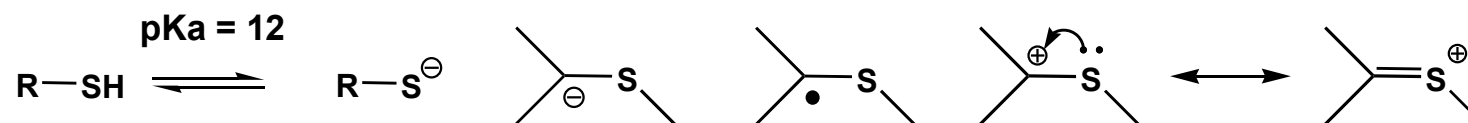


$\chi_S = 2.58$



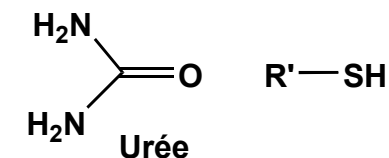
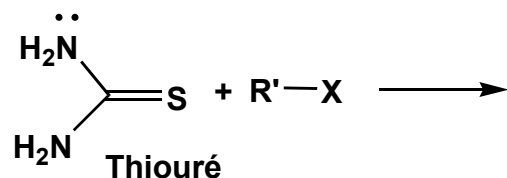
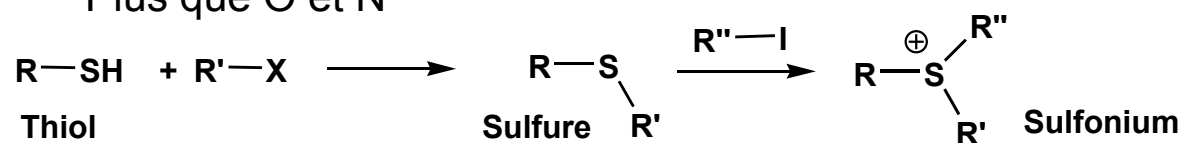
$\chi_O = 3.44$ ($\chi_C = 2.55$)

■ 2.1.1 Stabilisation des charges : polarisabilité du soufre



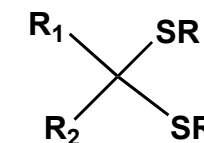
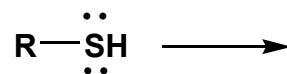
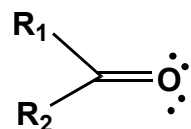
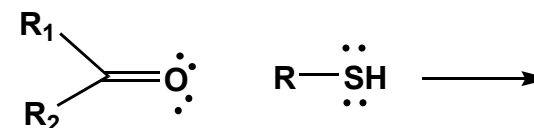
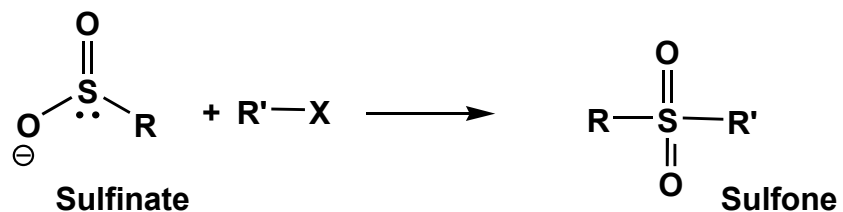
■ 2.1.2 S Nucléophile

Plus que O et N

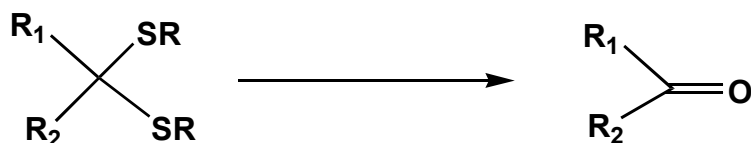


2 Soufre

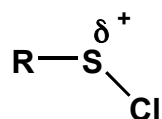
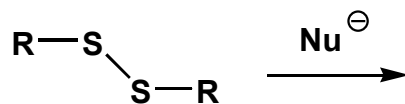
2.1.2 S Nucléophile



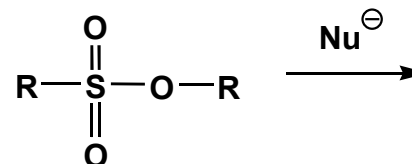
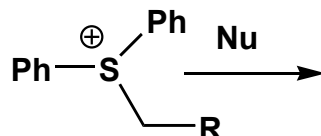
Thioacétal
Dithiane



2.1.3 S Electrophile

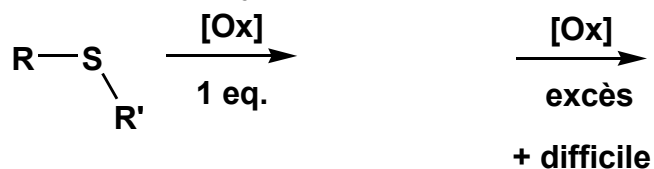


2.1.3 Bons GP à base de soufre



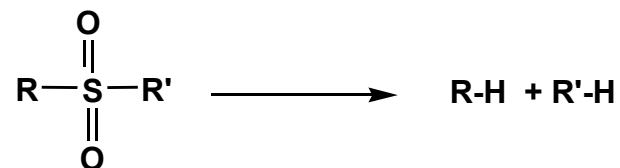
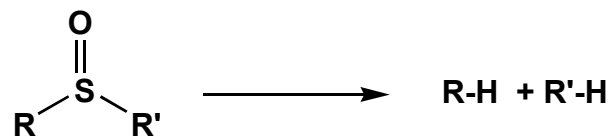
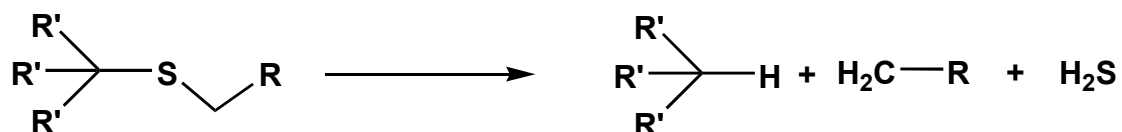
2 Soufre

■ 2.1.4 S s'oxyde facilement

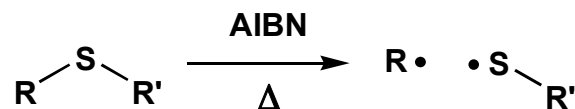


Ox : NaIO₄, mCPBA, H₂O₂, CrO₃, KMnO₄, KHSO₅

■ 2.1.5 La liaison C-S se réduit facilement



■ 2.1.6 Rupture homolytique de la liaison C-S



2 Soufre

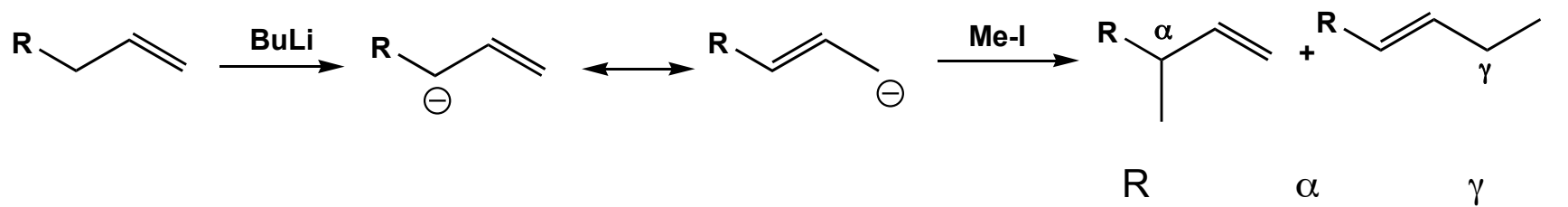
2.2 Les carbanions en α du soufre

2.2.1 Formation de carbanions

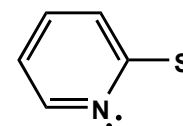
□ *Déprotonation*

□ *Addition nucléophile*

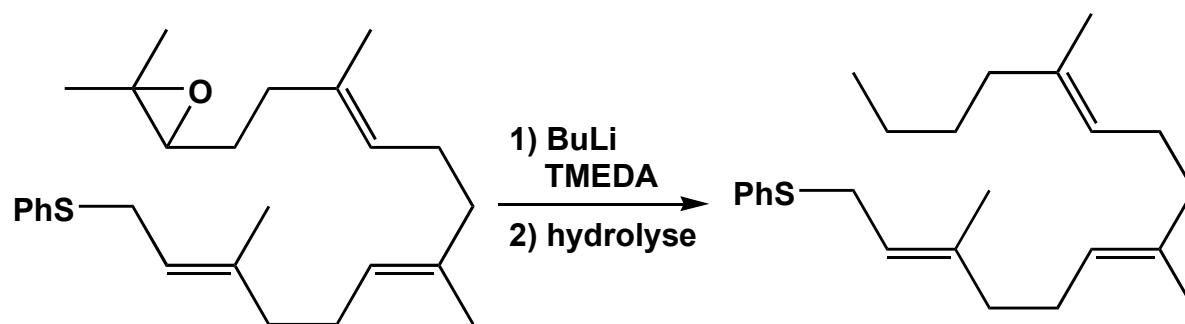
2.2.2 Réactions d'alkylation



PhS



Alkyl
(encombré)

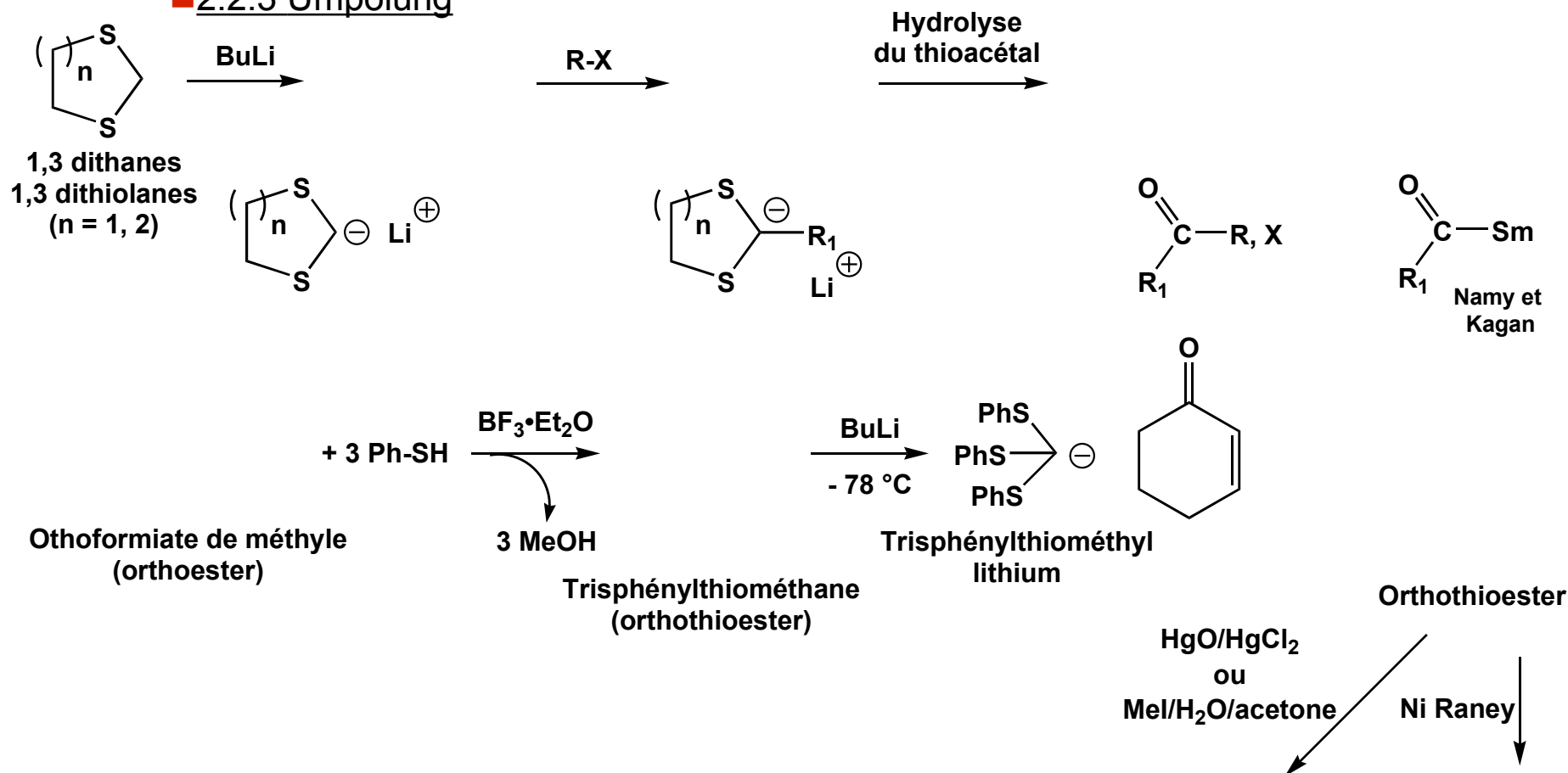


Attaque nucléophile aussi possible cétone, aldéhyde...

2 Soufre

2.2 Les carbanions en α du soufre

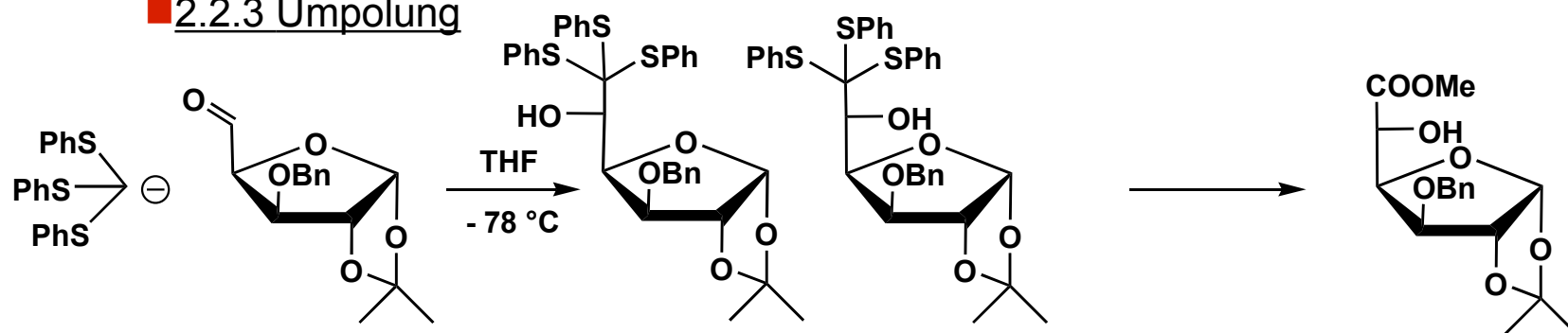
2.2.3 Umpolung



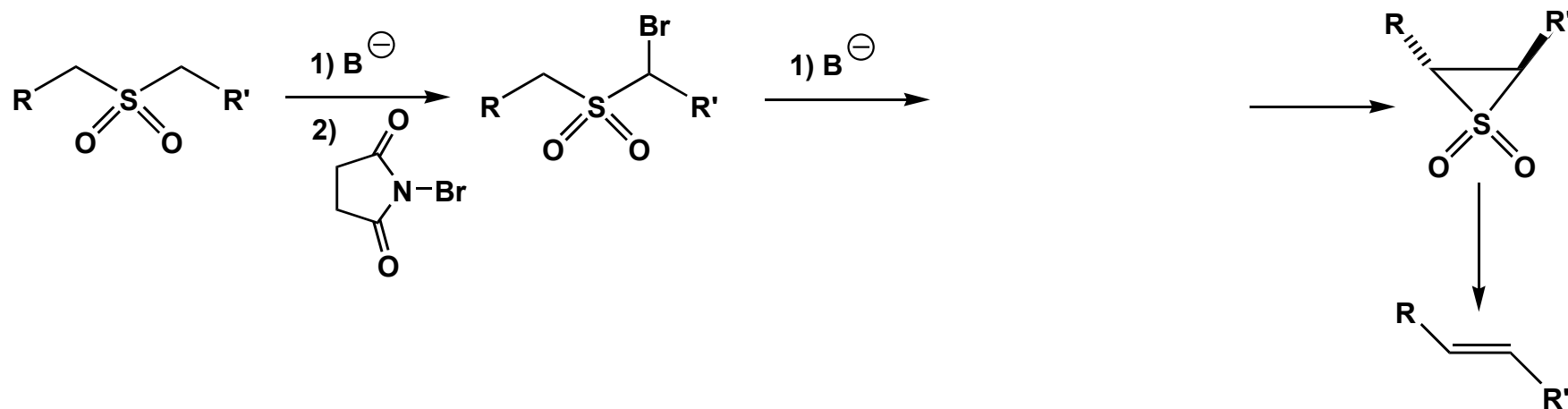
2 Soufre

2.2 Les carbanions en α du soufre

2.2.3 Umpolung



2.2.4 Elimination de Ramberg Bäcklund

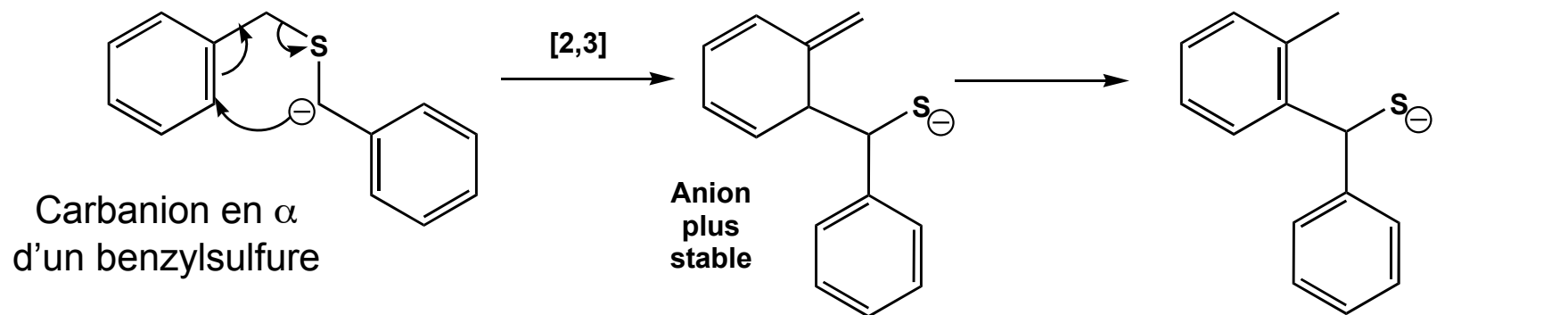


2 Soufre

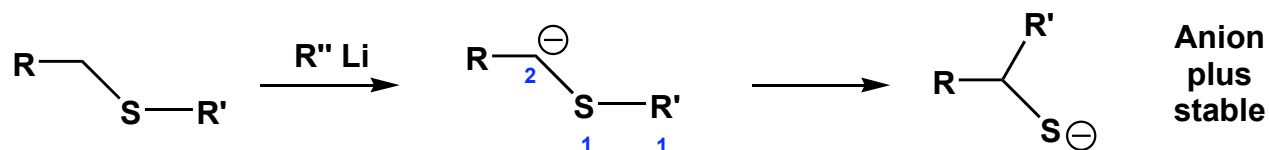
2.2 Les carbanions en α du soufre

2.2.5 Réarrangements [m,n]

a) Réarrangement [2,3] de Sommelet



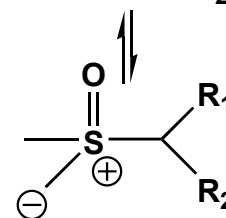
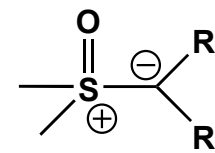
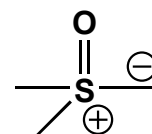
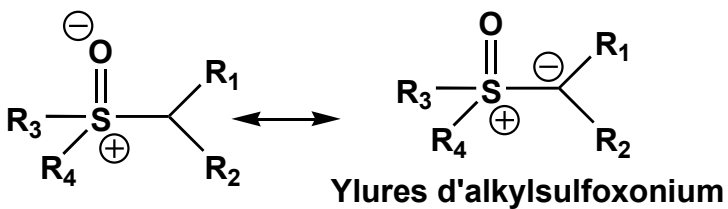
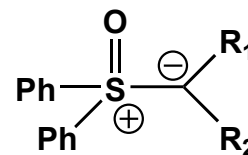
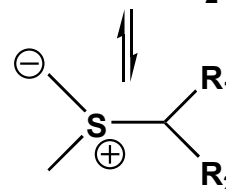
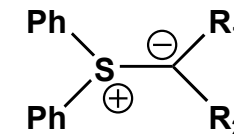
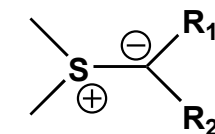
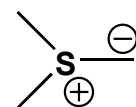
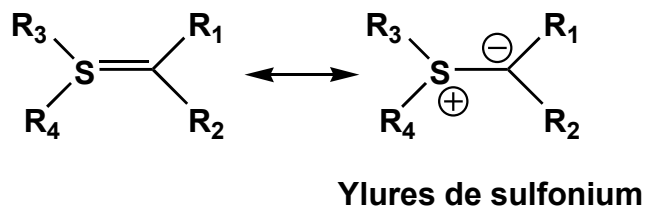
b) Réarrangement [1,2] de Wittig



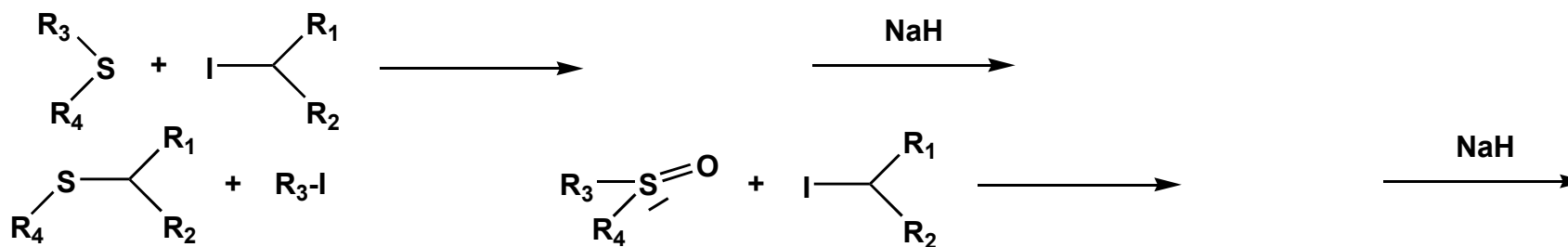
2 Soufre

2.2 Les carbanions en α du soufre

2.2.7 Ylures de soufre



a) Préparation

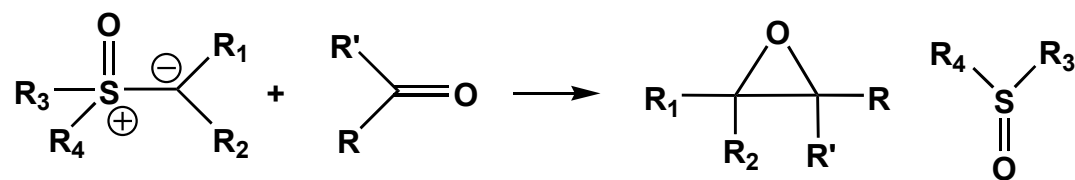
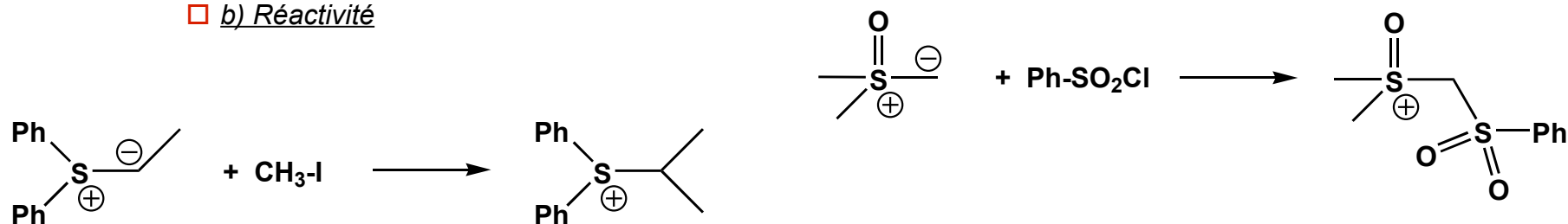


2 Soufre

2.2 Les carbanions en α du soufre

2.2.7 Ylures de soufre

b) Réactivité

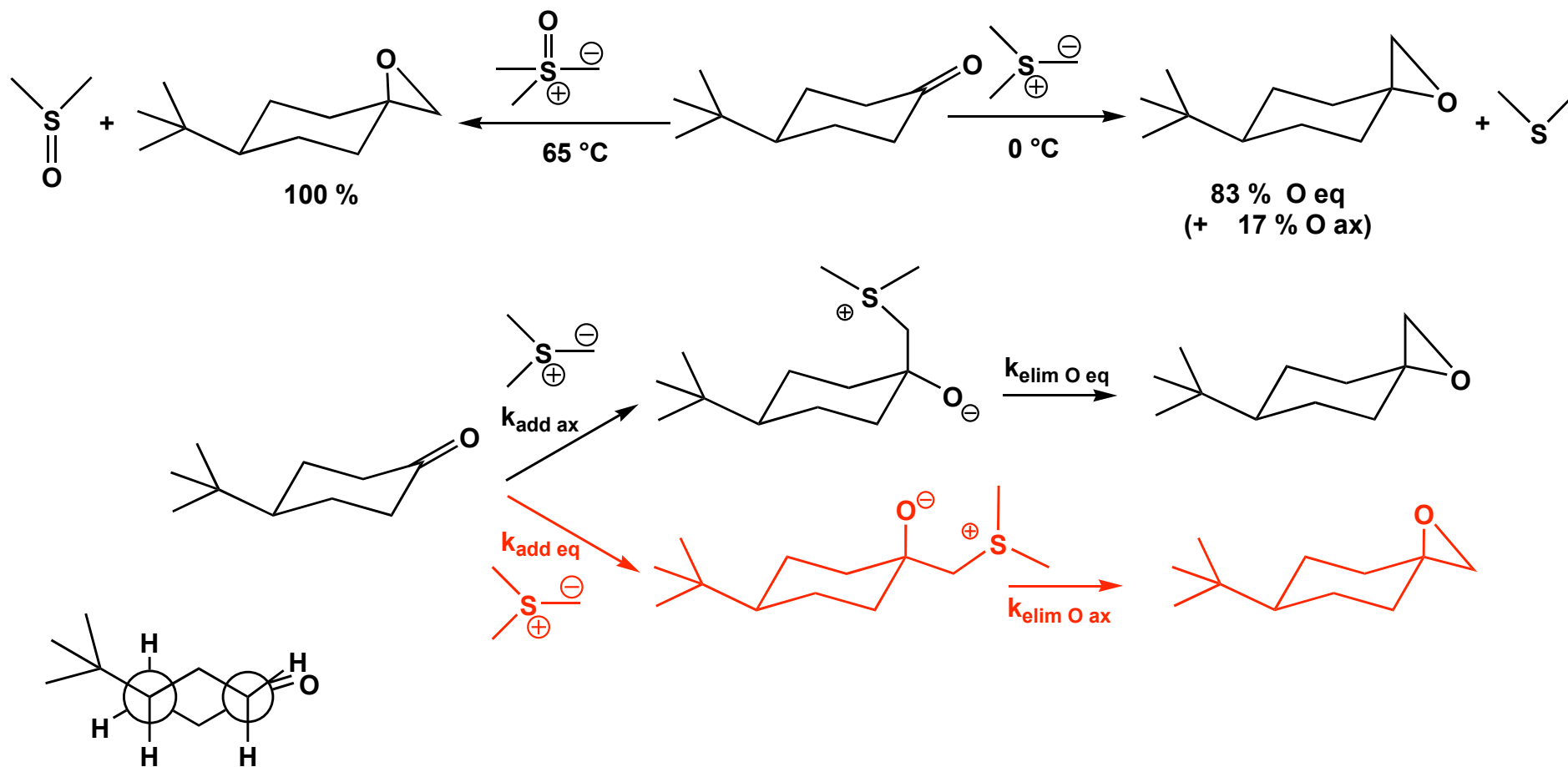


2 Soufre

2.2 Les carbanions en α du soufre

2.2.7 Ylures de soufre

c) Diastéréosélectivité

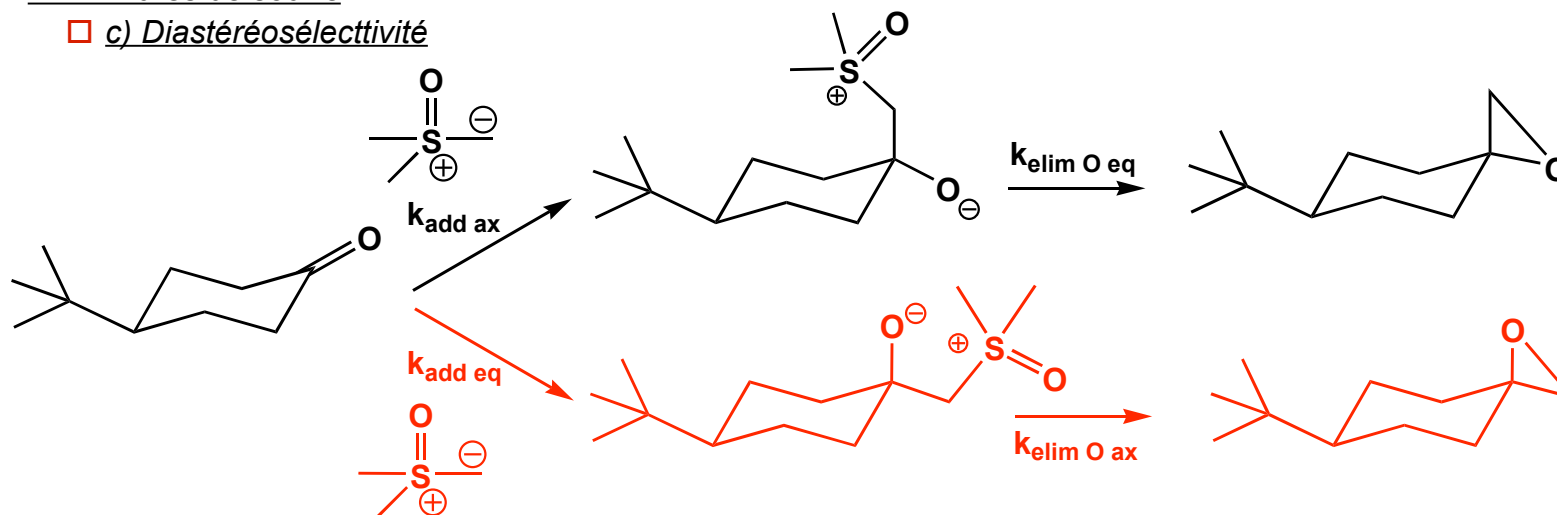


2 Soufre

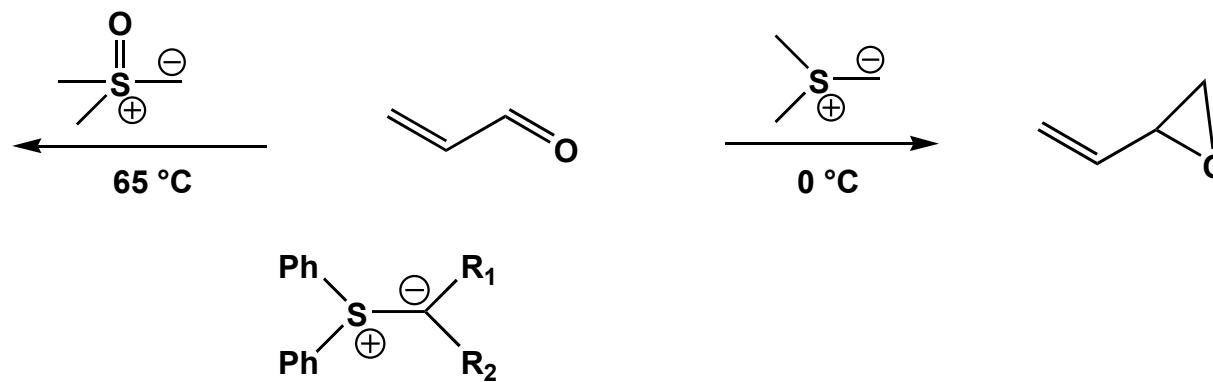
2.2 Les carbanions en α du soufre

2.2.7 Ylures de soufre

c) Diastéréosélectivité



d) Régiosélectivité



2 Soufre

2.2 Les carbanions en α du soufre

2.2.7 Ylures de soufre

e) Réarrangements des ylures de sulfonium

■ Réarrangement [1,2] de Stevens



■ Réarrangement [2,3] de Sommelet-Hauser sur les ylures d'allylsulfonium



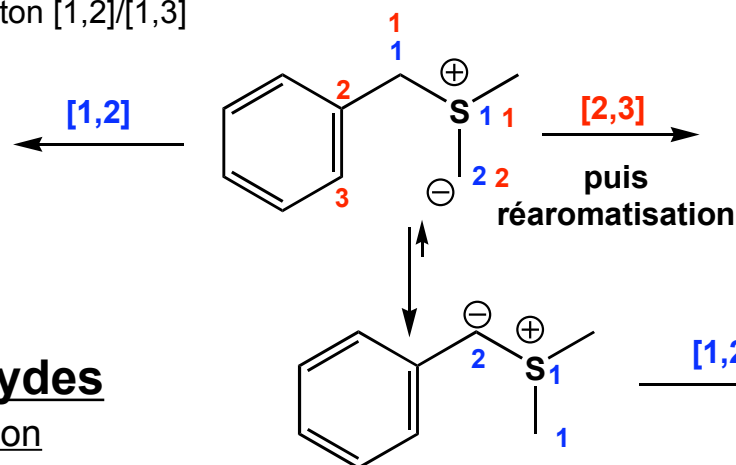
2 Soufre

2.2 Les carbanions en α du soufre

2.2.7 Ylures de soufre

e) Réarrangements des ylures de sulfonium

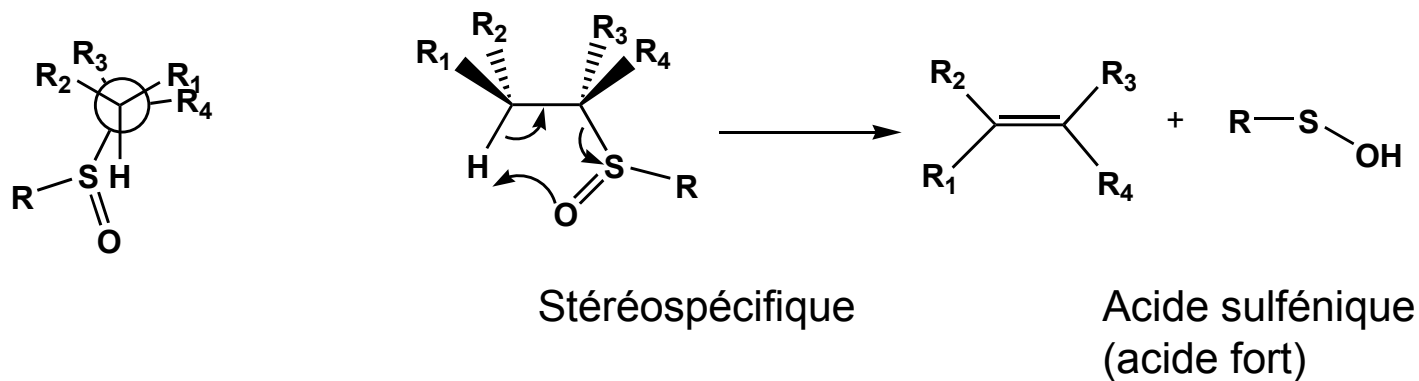
Compétition [1,2]/[1,3]



2.3 Les sulfoxydes

2.3.1 Préparation

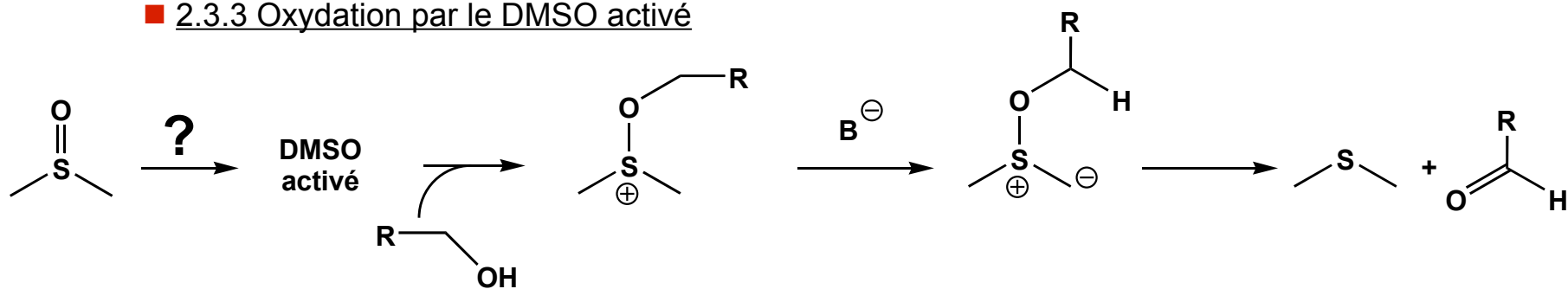
2.3.2 β -élimination



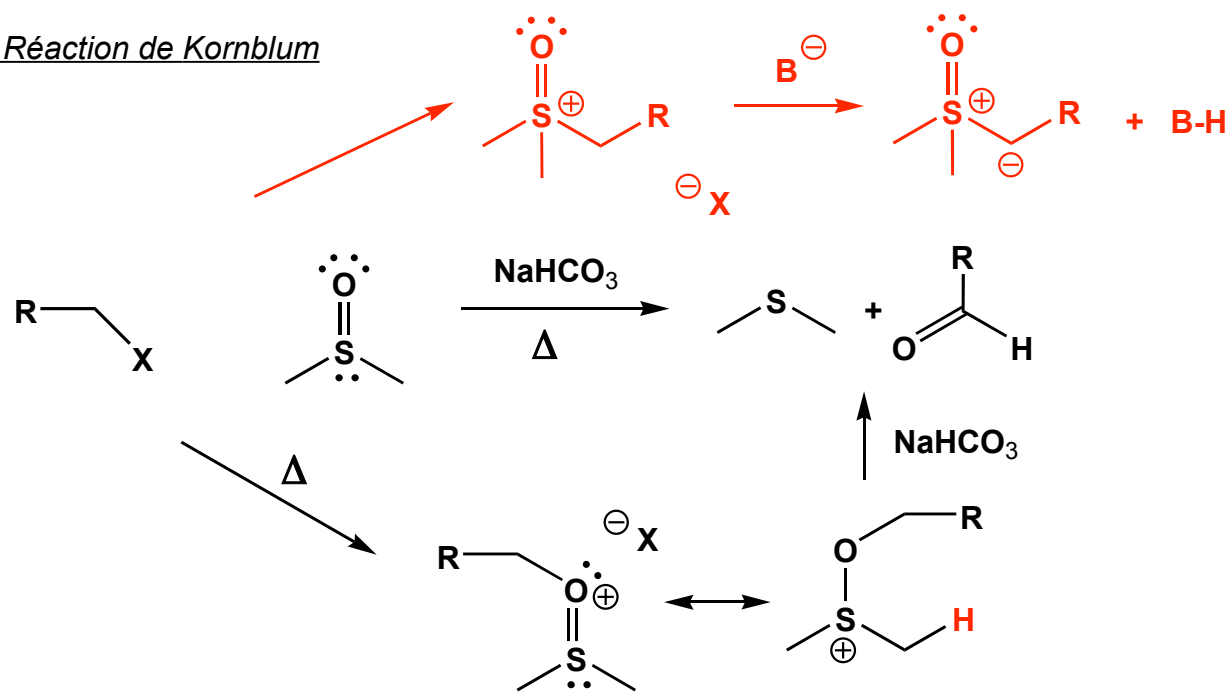
2 Soufre

□ 2.3 Les sulfoxydes

■ 2.3.3 Oxydation par le DMSO activé



□ a) Réaction de Kornblum

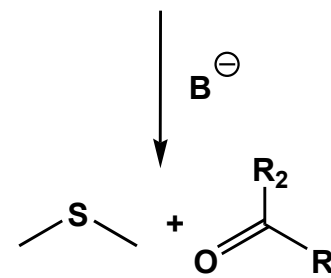
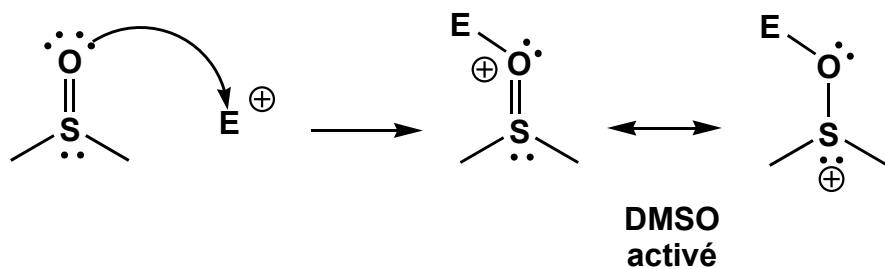


2 Soufre

□ 2.3 Les sulfoxydes

■ 2.3.3 Oxydation par le DMSO activé

□ *b) Activation du DMSO*

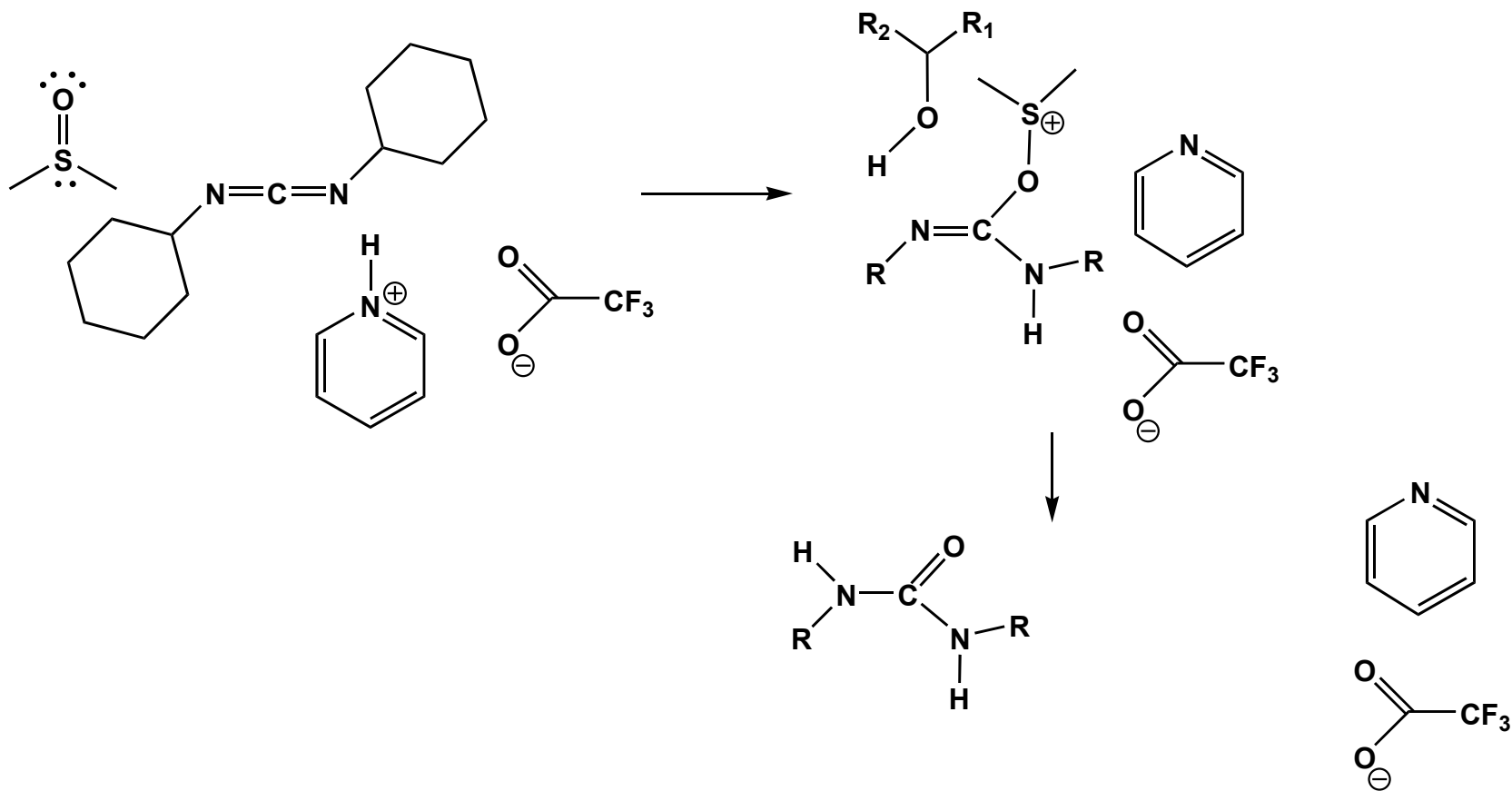


2 Soufre

2.3 Les sulfoxydes

2.3.3 Oxydation par le DMSO activé

c) Oxydation de Pfitzner-Moffat : DCC/trifluoroacétate de pyridinium

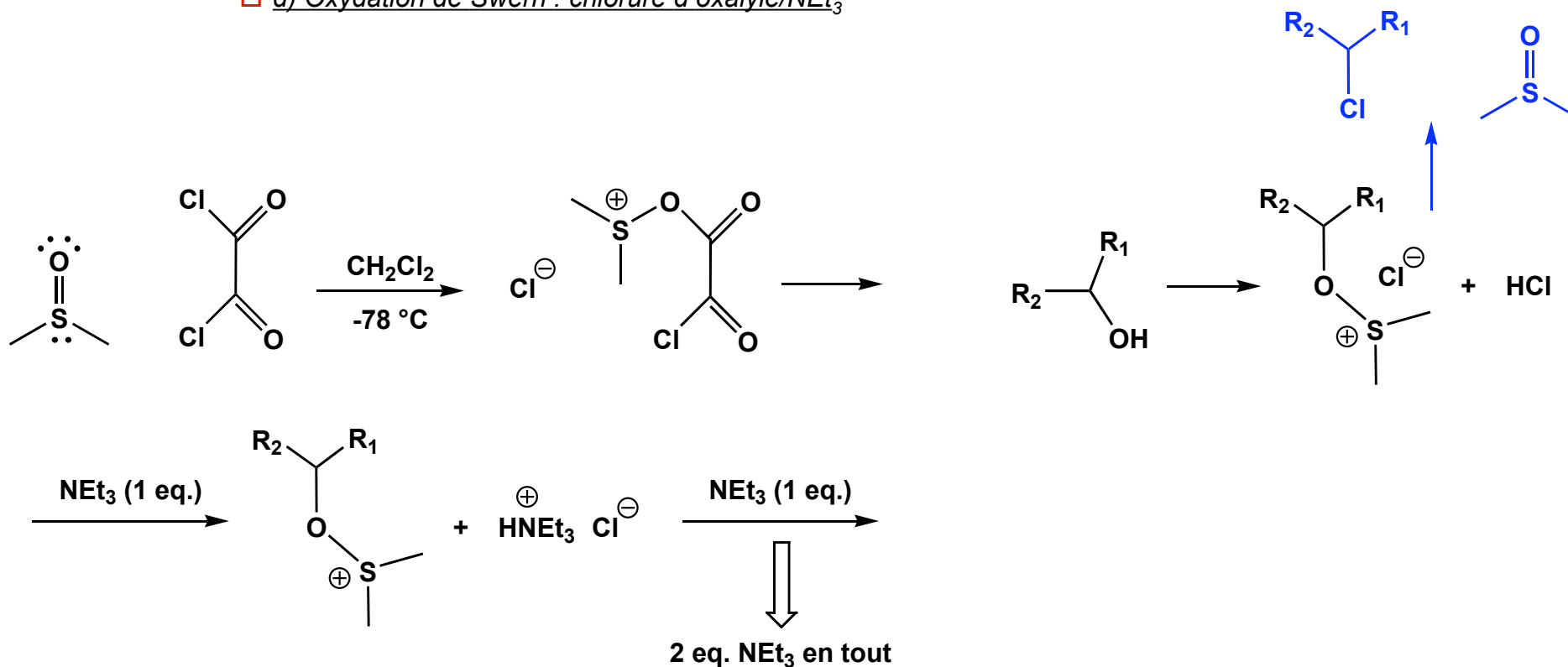


2 Soufre

□ 2.3 Les sulfoxydes

■ 2.3.3 Oxydation par le DMSO activé

□ d) Oxydation de Swern : chlorure d'oxalyle/ NEt_3



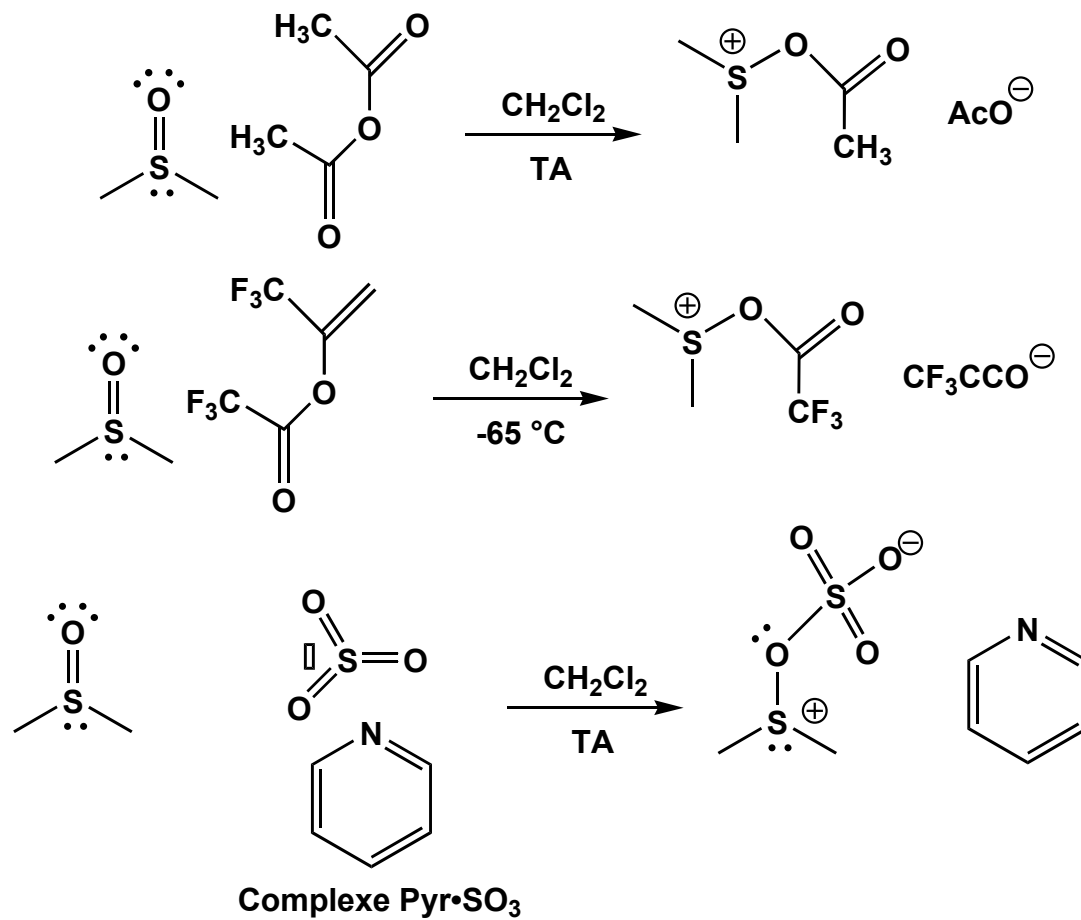
2 Soufre

2.3 Les sulfoxydes

2.3.3 Oxydation par le DMSO activé

e) Autres activations

Albright
Goldman

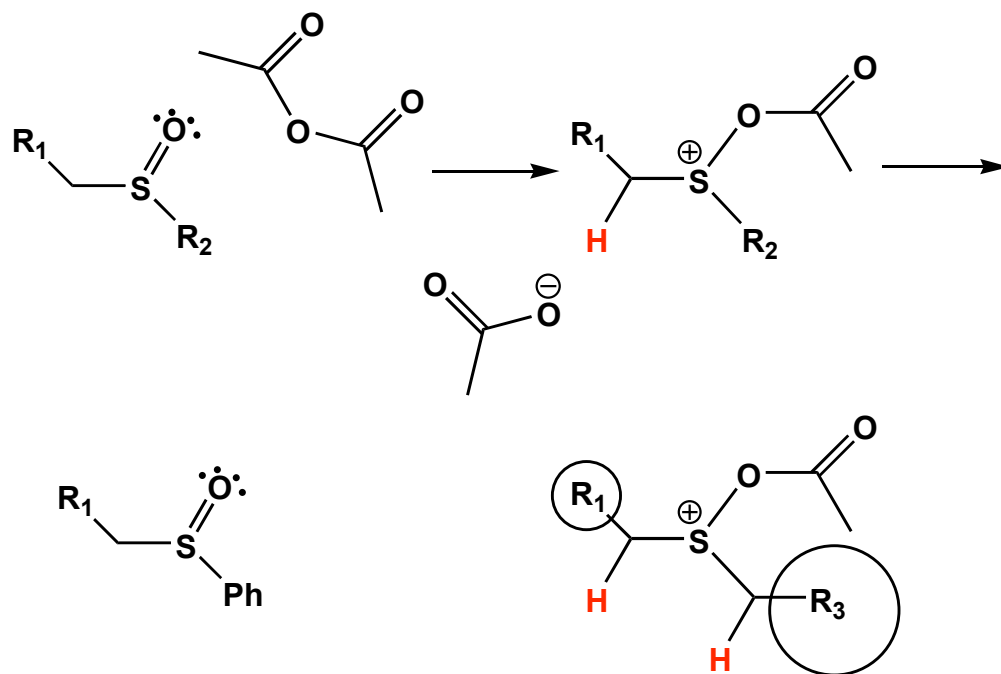


2 Soufre

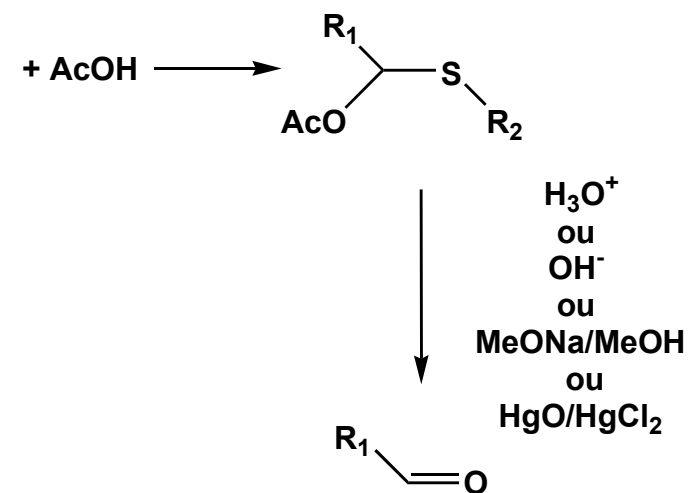
2.3 Les sulfoxydes

2.3.4 Réaction de Pummerer

a) *Génération de l'intermédiaire de Pummerer en milieu basique*



Intermédiaire de Pummerer :
méthylènesulfonium



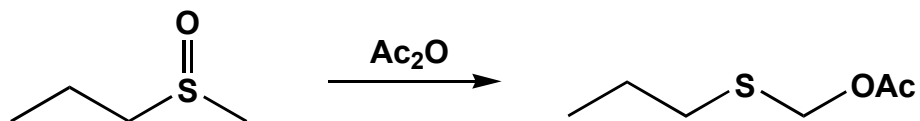
2 Soufre

□ 2.3 Les sulfoxydes

■ 2.3.4 Réaction de Pummerer

Intermédiaire de Pummerer :
méthylènesulfonium

□ a) *Génération de l'intermédiaire de Pummerer en milieu basique*

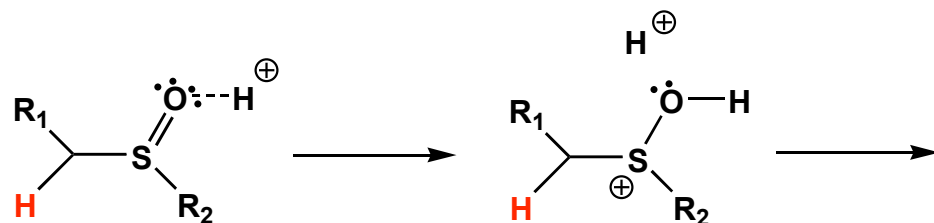


2 Soufre

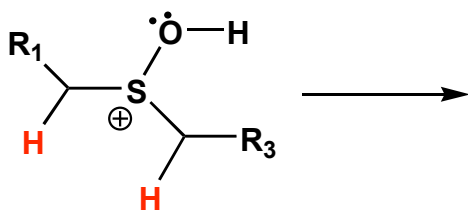
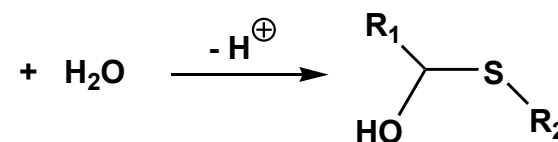
2.3 Les sulfoxydes

2.3.4 Réaction de Pummerer

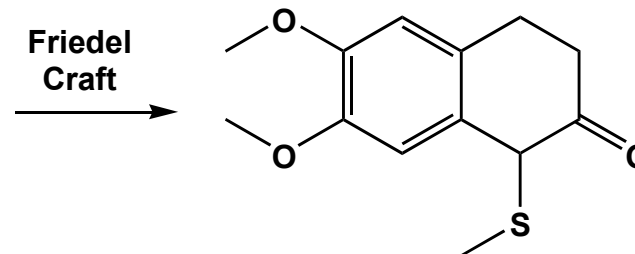
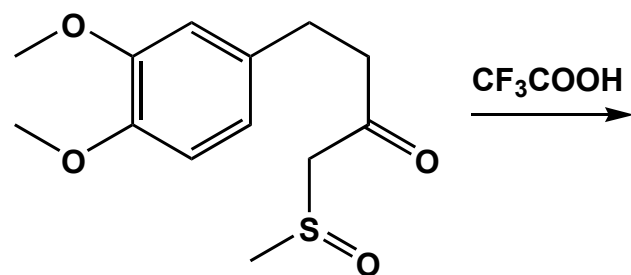
b) Génération de l'intermédiaire de Pummerer en milieu acide



Intermédiaire de Pummerer :
méthylènesulfonium



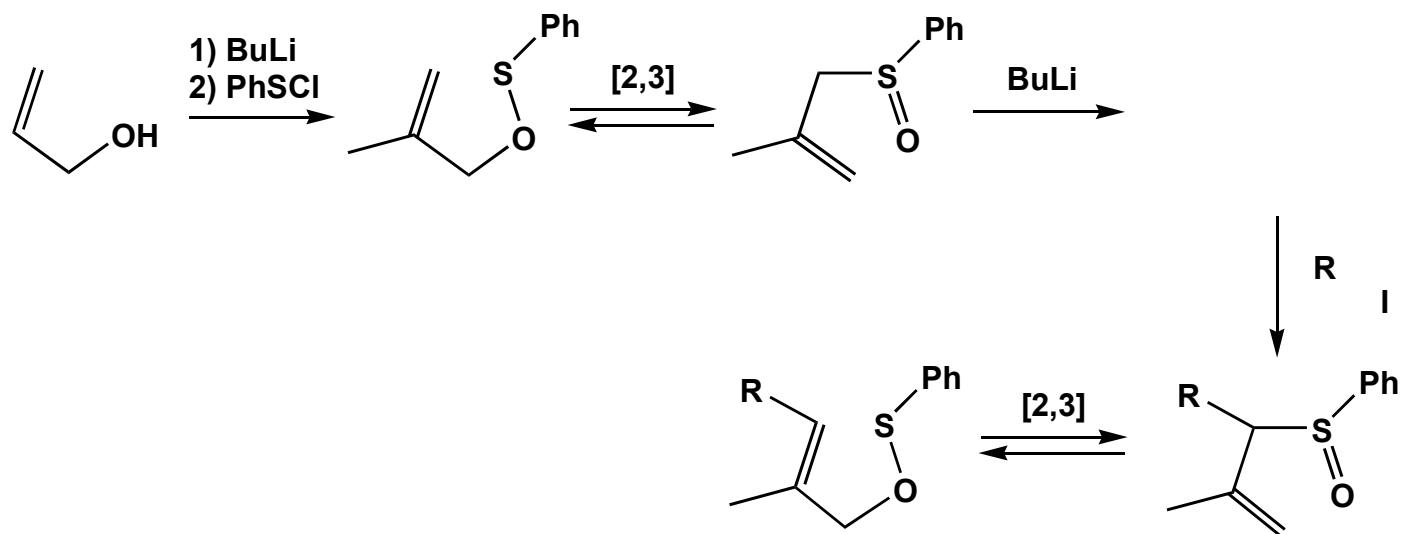
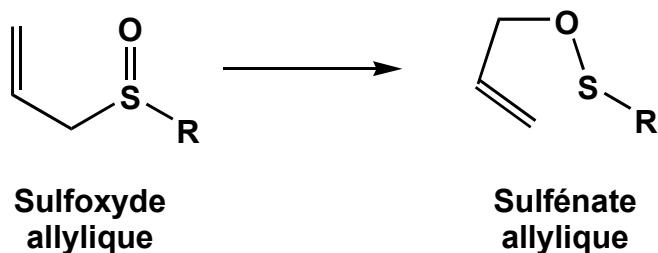
Contrôle
thermodynamique



2 Soufre

2.3 Les sulfoxydes

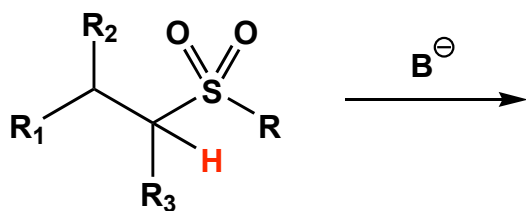
2.3.4 Réarrangement [2,3] d'Evans-Grieco



2 Soufre

□ 2.4 Les sulfones

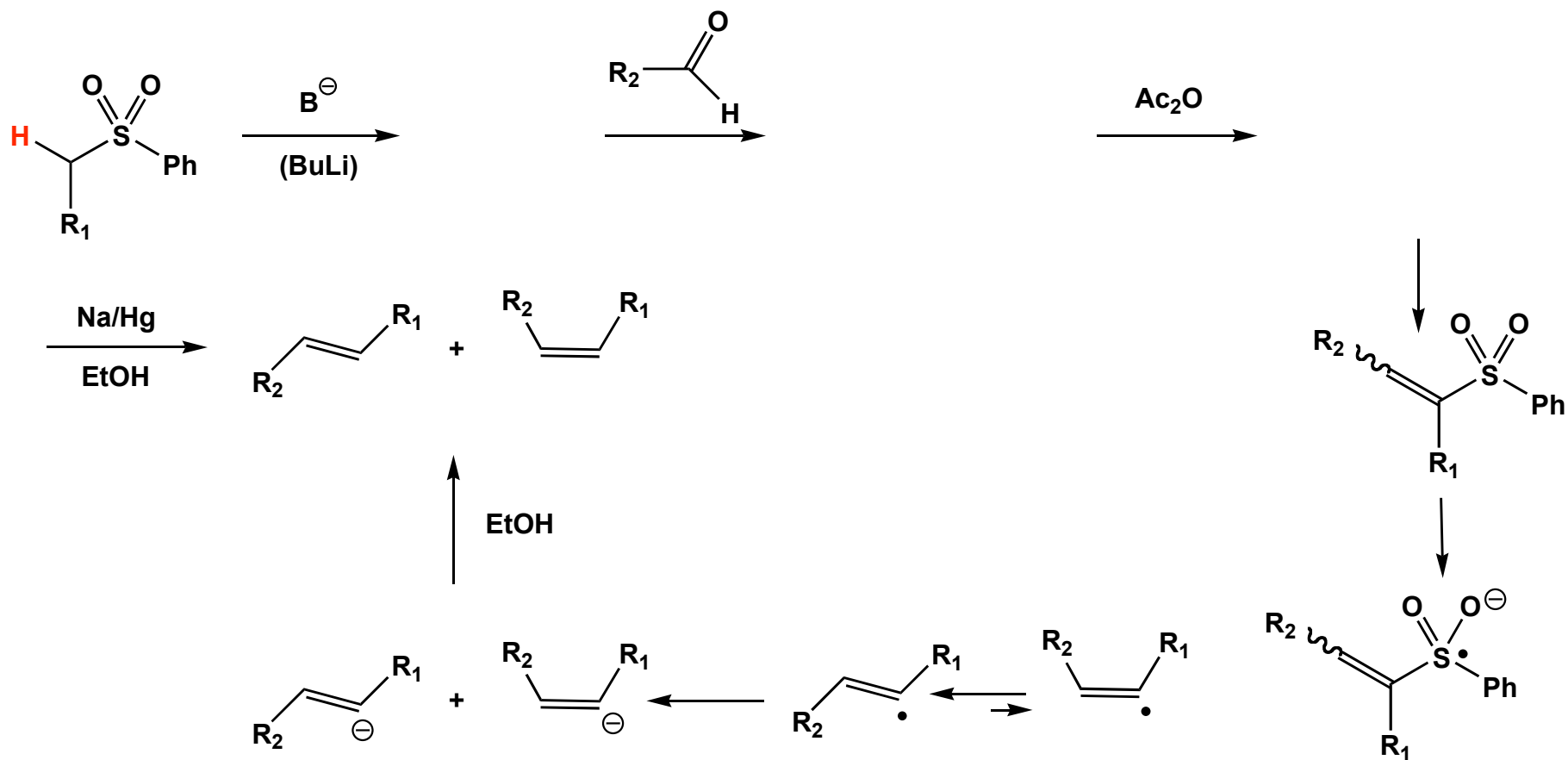
- 2.4.1 Préparation
- 2.4.2 β-élimination



2 Soufre

□ 2.4 Les sulfones

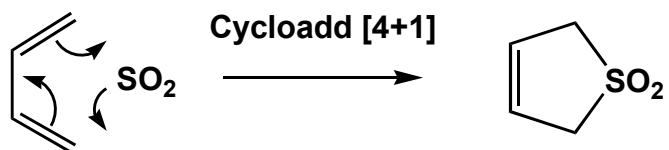
■ 2.4.3 Réaction d'oléfination de Julia



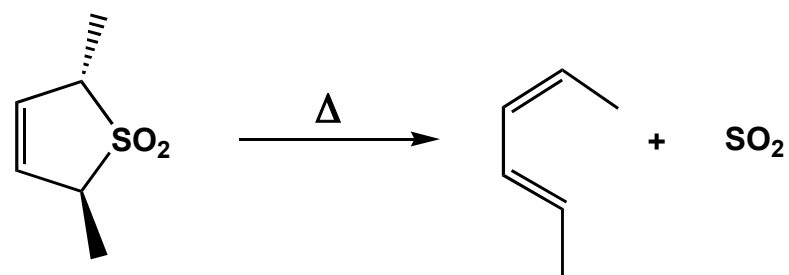
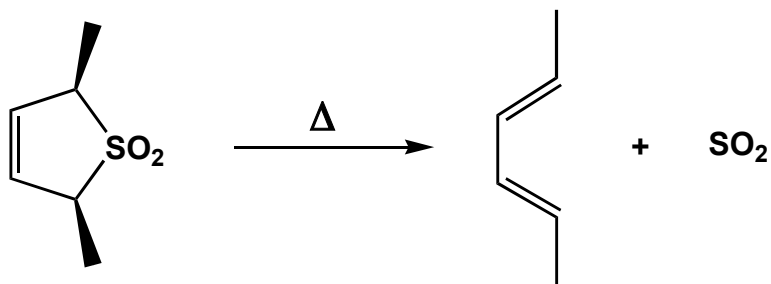
2 Soufre

□ 2.4 Les sulfones

■ 2.4.4 Extrusion de SO₂



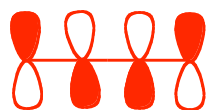
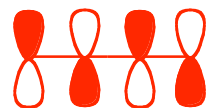
Stéréospécifique



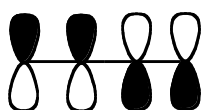
2 Soufre

2.4 Les sulfones

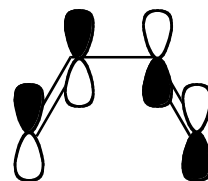
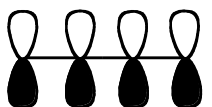
2.4.4 Extrusion de SO₂



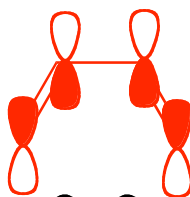
LUMO/BV



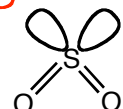
HOMO/HO



LUMO/BV

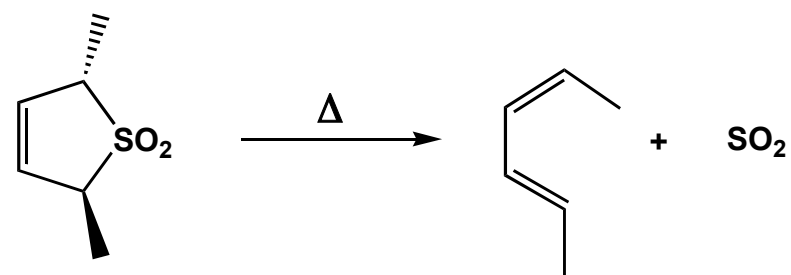
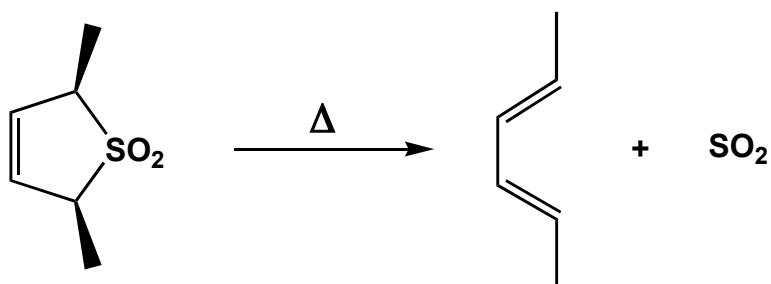


LUMO/BV



HOMO/HO

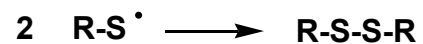
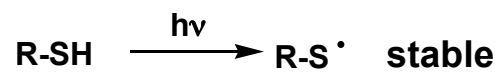
SO₂



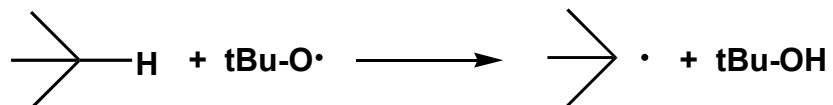
2 Soufre

□ 2.5 Réactions radicalaires

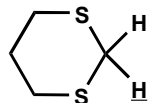
■ 2.5.1 Radical soufre



■ 2.5.2 Radical soufre



Ph-CH₃
Ph-CH₂-CH₃
Ph-CH-(CH₃)₂
Et-S-CH₂-CH₃



1

Ph-S-CH₃
Ph-O-CH₃
Ph-SO₂-CH₃