

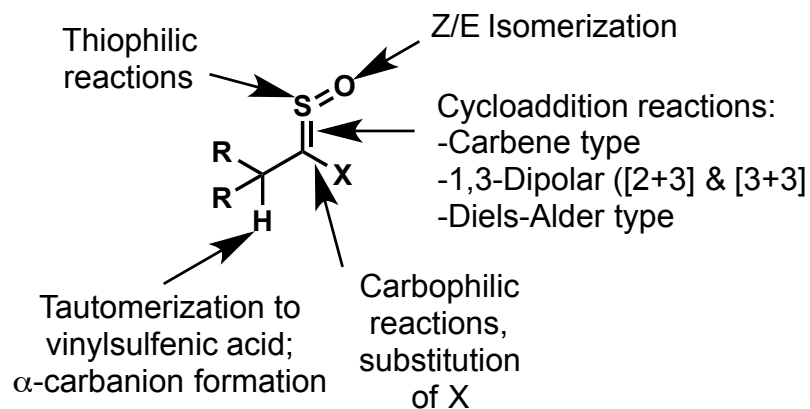
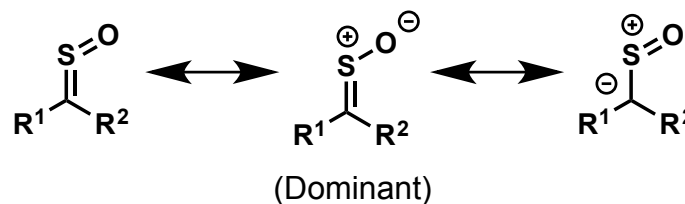
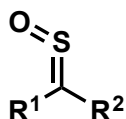
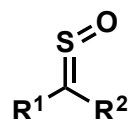


SULFINES

John Gurak

3/30/17

General Characteristics



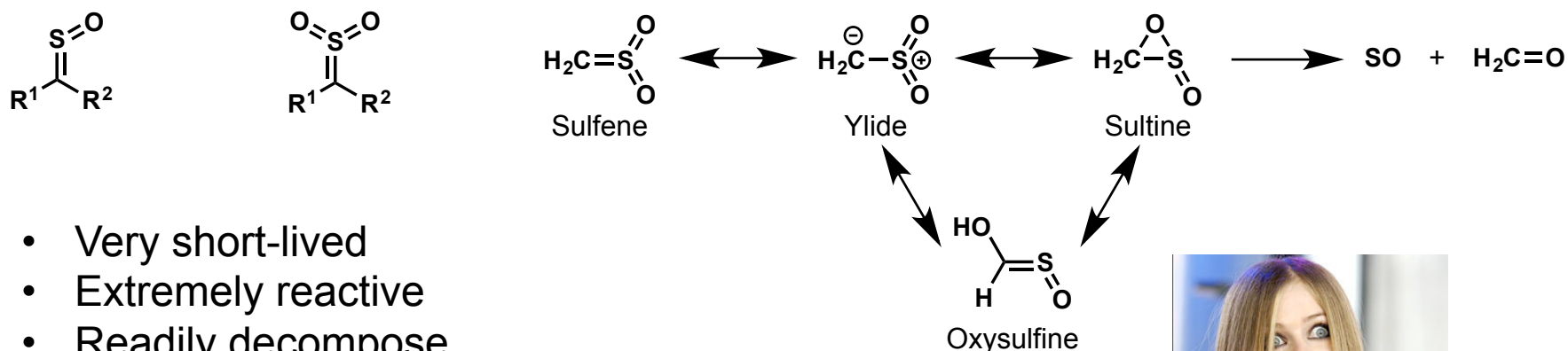
- C–S length is 1.62 Å
- S–O length is 1.46 Å
- C–S–O angle is 114°

- Planar
- Short-lived
- Highly reactive

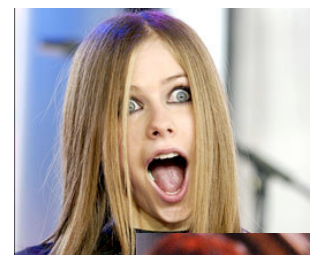


ck
Calvin Klein

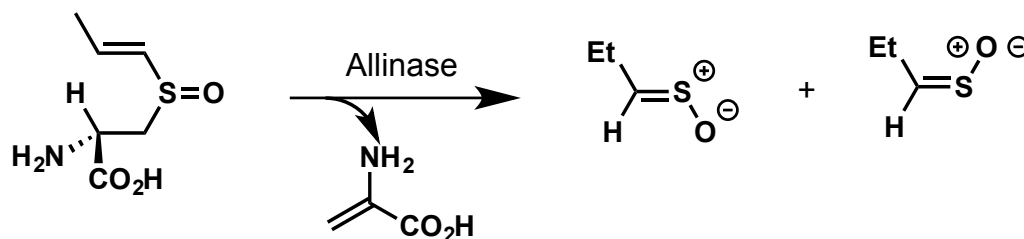
Sulfenes – A Brief Aside



- Very short-lived
- Extremely reactive
- Readily decompose
- Never isolated
- Calculations show:
 - Planar
 - Large dipole moment on C=S
 - Electronegative substituents destabilize while electropositive substituents stabilize sulfene



Naturally Occurring Sulfines



Virtanen (1961)
 Wilkens (1961)
 Brodnitz & Pascale (1971)
 Block (1979)

- *Allium cepa* (onion)
- Lachrymator

Virtanen, A. I. *Angew. Chem. Int. Ed.* **1962**, 1, 299.

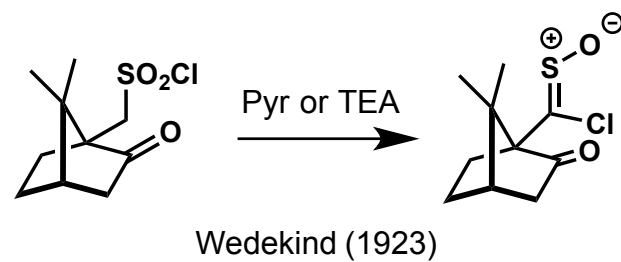
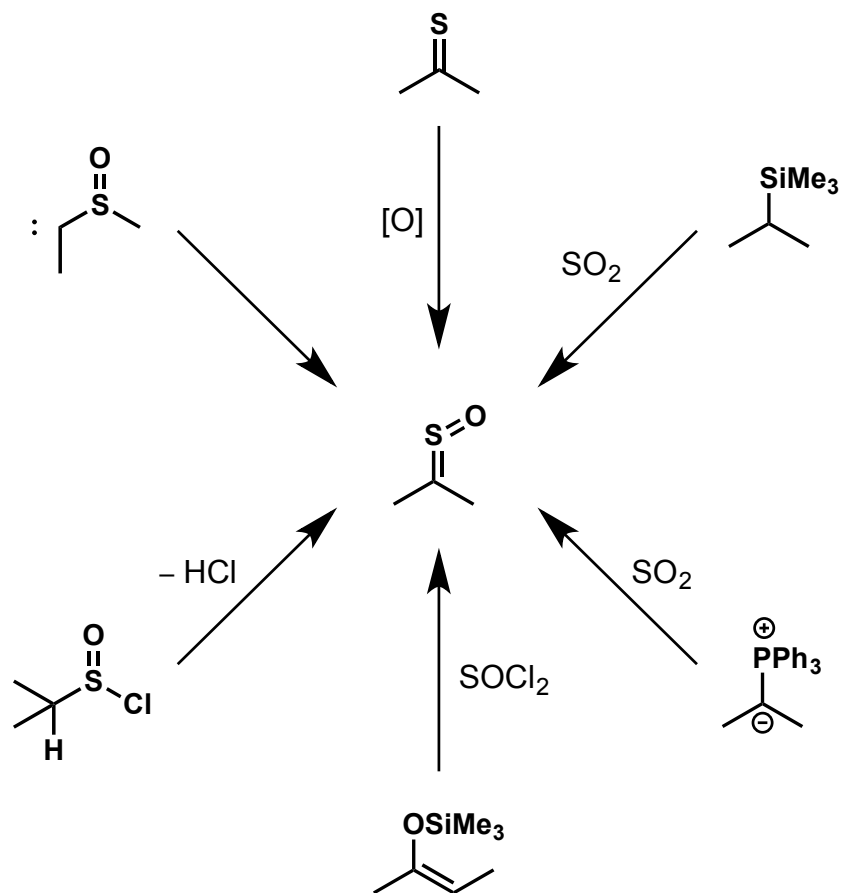
Virtanen, A. I. *Phytochemistry* **1965**, 4, 207.

Wilkens, W. F. Ph. D. thesis, Cornell University (Ithaca, New York), 1961.

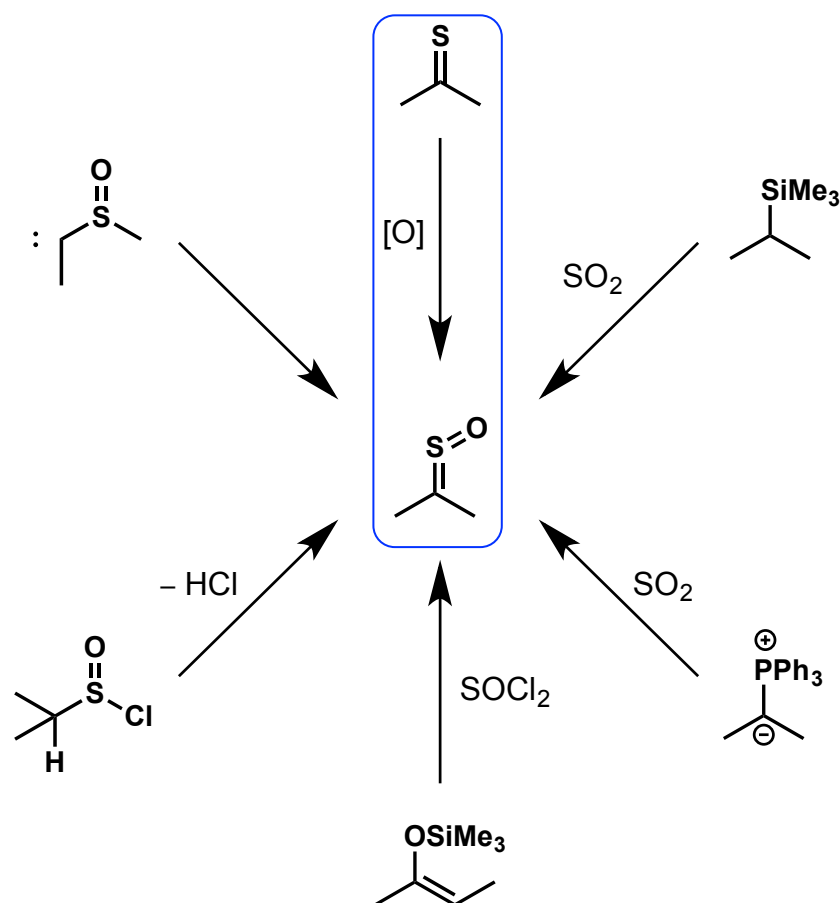
Brodnitz, M. H.; Pascale, J. V. *J. Agric. Food Chem.* **1971**, 19, 269.

Block, E.; Penn, R. E.; Reville, L. K. *J. Am. Chem. Soc.* **1979**, 101, 2200.

Preparation of Sulfoxes

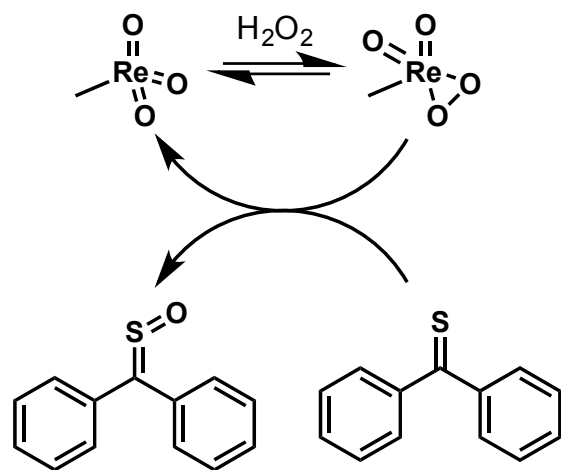
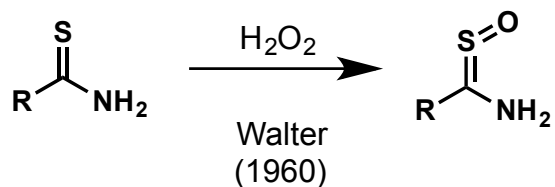


Preparation of Sulfoxes – Oxidation

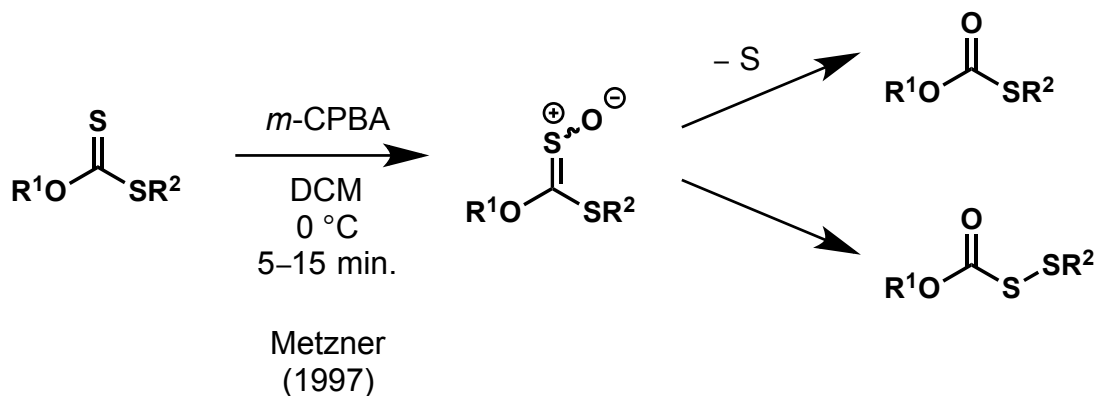


- Oxidants:
 - *m*-CPBA
 - Hydrogen Peroxide
 - Monophthalic Acid
 - DMDO
 - Singlet Oxygen
 - Ozone

Preparation of Sulfoxes – Oxidation



Espenson
(1999)

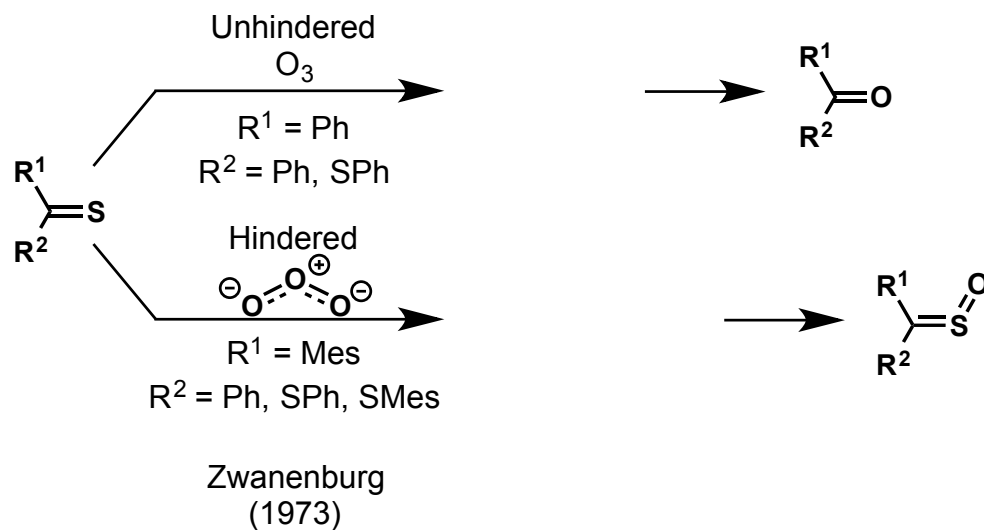


Walter, W. *Justus Liebigs Ann. Chem.* **1960**, 633, 35.

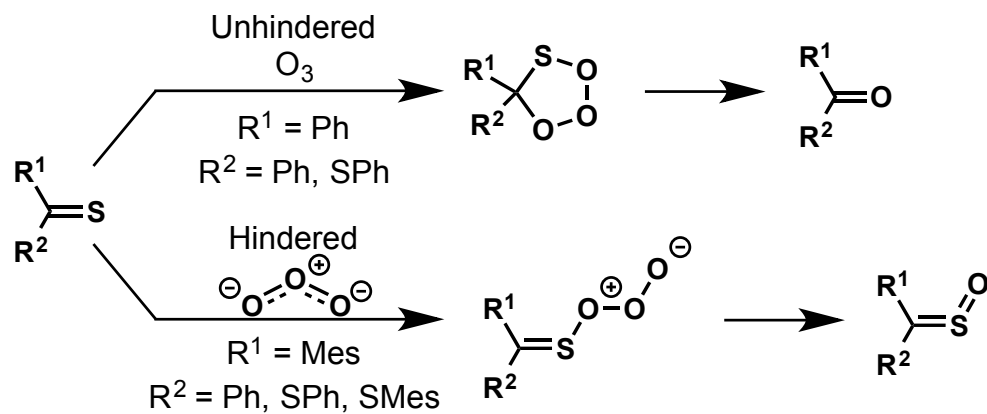
Marriere, E.; Chevie, D.; Metzner, P. J. *Chem. Soc., Perkin Trans. 1* **1997**, 2019.

Huang, R.; Espenson, J. H. *J. Org. Chem.* **1999**, 64, 6935.

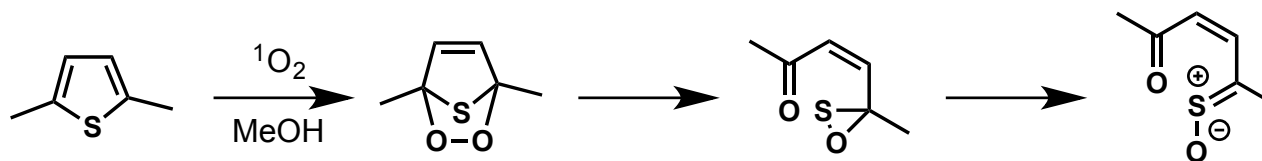
Preparation of Sulfoxes – Oxidation



Preparation of Sulfoxes – Oxidation

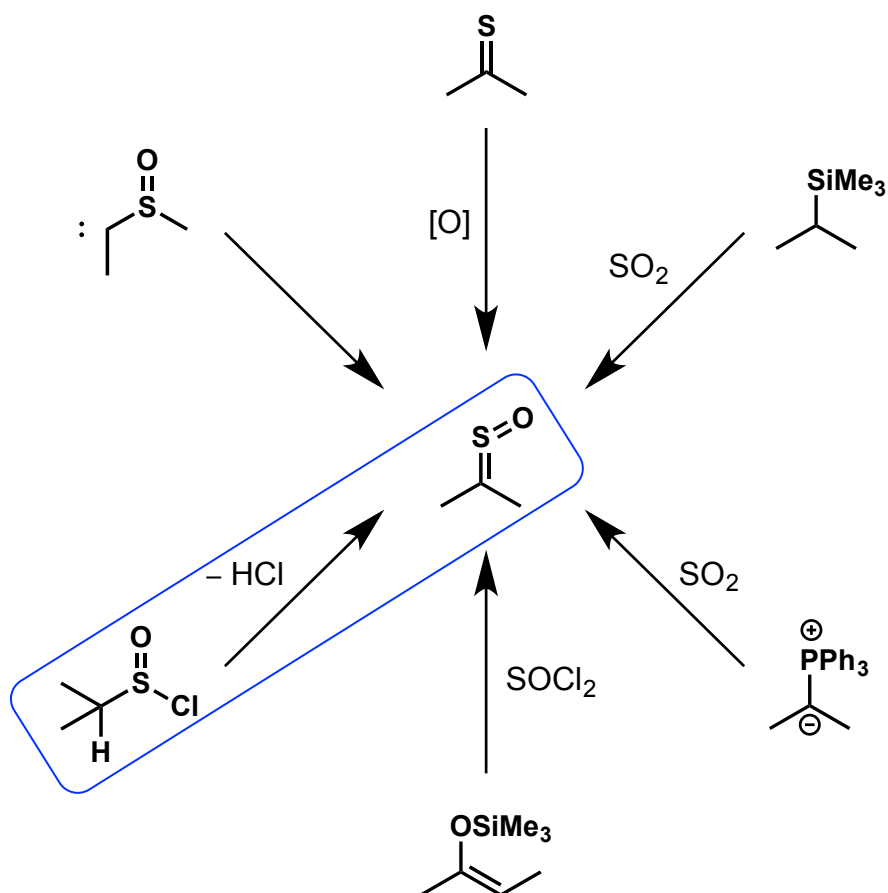


Zwanenburg
(1973)



Schlessinger
(1970)

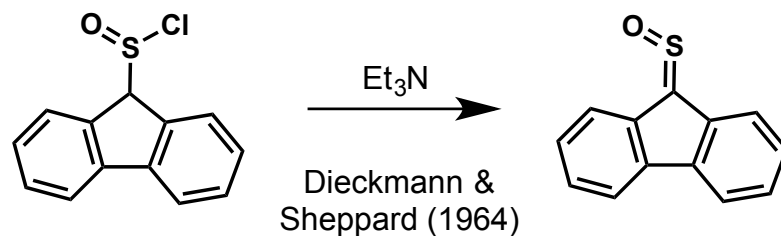
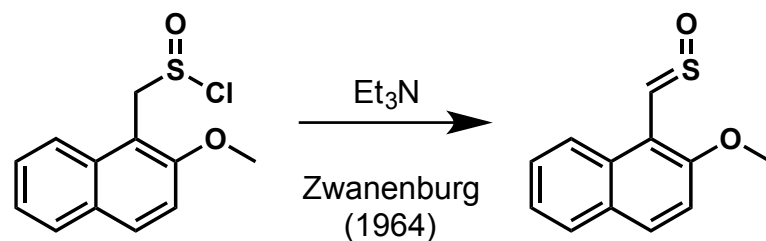
Preparation of Sulfines – Elimination



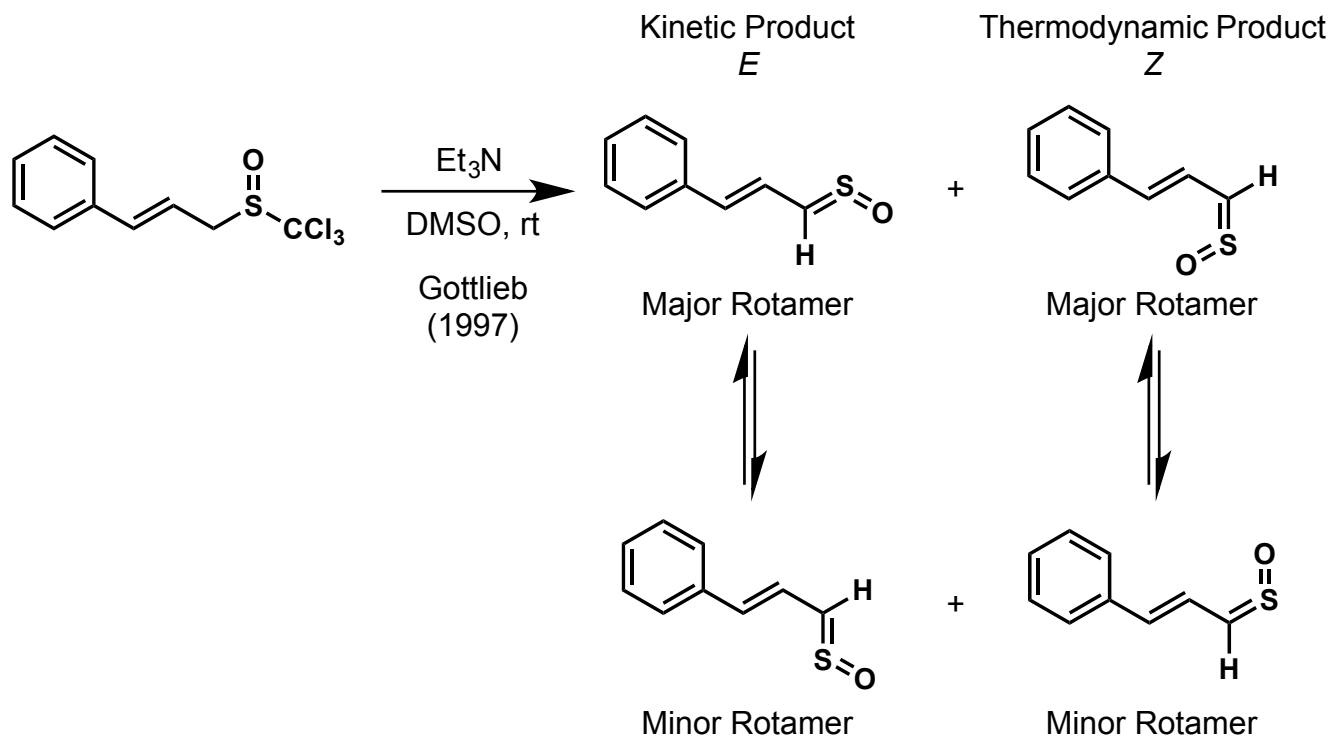
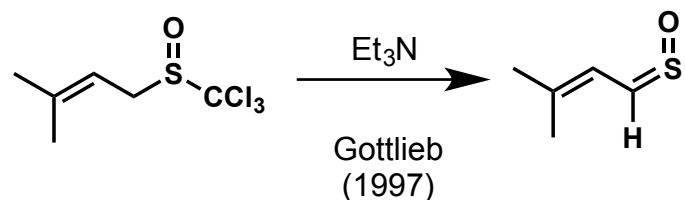
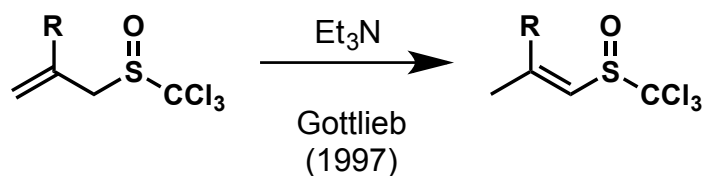
- Leaving Groups:

- Cl⁻
- ⁻CCl₃
- ⁻OTMS
- ⁻OMe
- ⁻NPhth

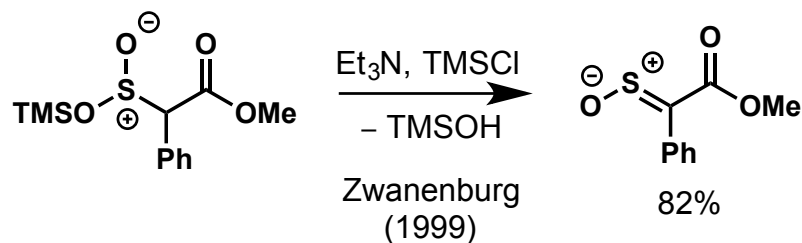
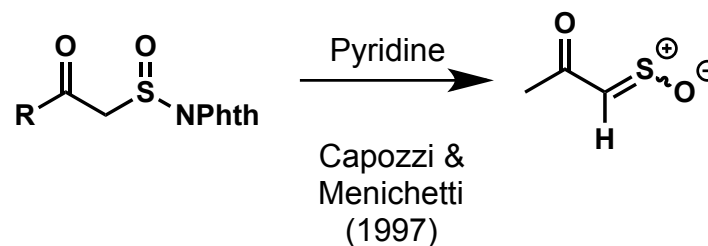
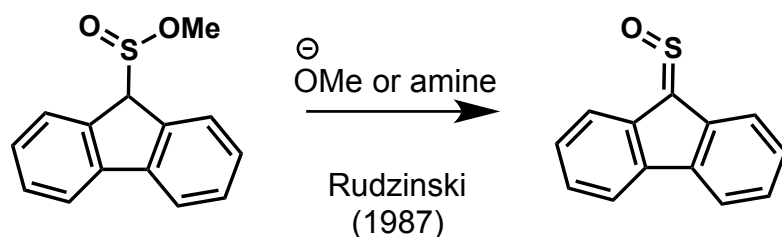
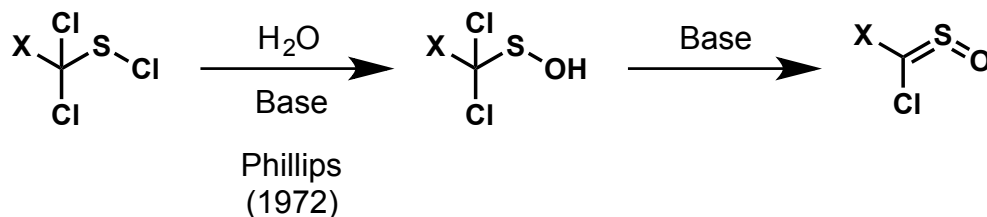
Preparation of Sulfines – Elimination



Preparation of Sulfines – Elimination



Preparation of Sulfines – Elimination



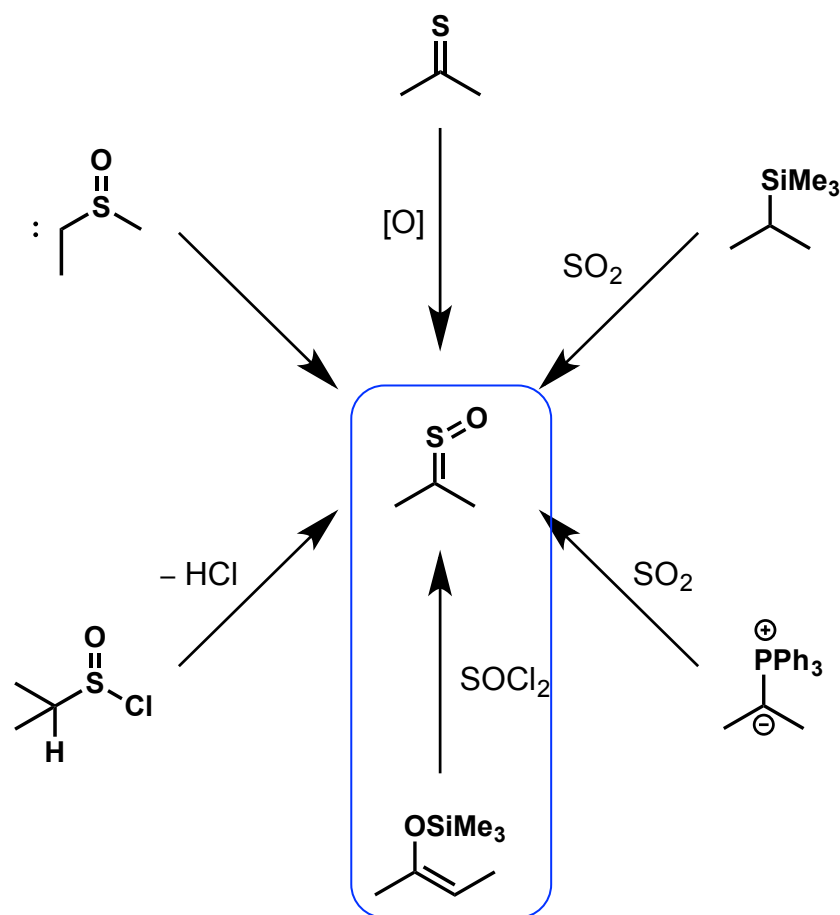
Phillips, W. G.; Ratts, K. W. *J. Org. Chem.* **1972**, 37, 3818.

Kice, J. L.; Rudzinski, J. J. *J. Am. Chem. Soc.* **1987**, 109, 2414.

Capozzi, G.; Corti, A.; Menichetti, S.; Nativi, C. *Tetrahedron Lett.* **1997**, 38, 5041.

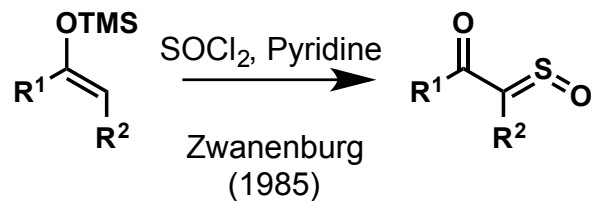
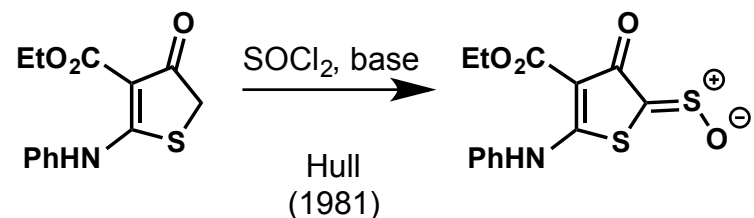
Zwanenburg, B.; Damen, T. J. G.; Philipse, H. J. F.; De Laet, R. C.; Lucassen, A. C. B. *Phosphorus, Sulfur, and Silicon* **1999**, 153, 119.

Preparation of Sulfines – Sulfenylation



- Formation of sulfinyl chloride, then dehydrohalogenation
- Base required for both tautomerization and elimination steps

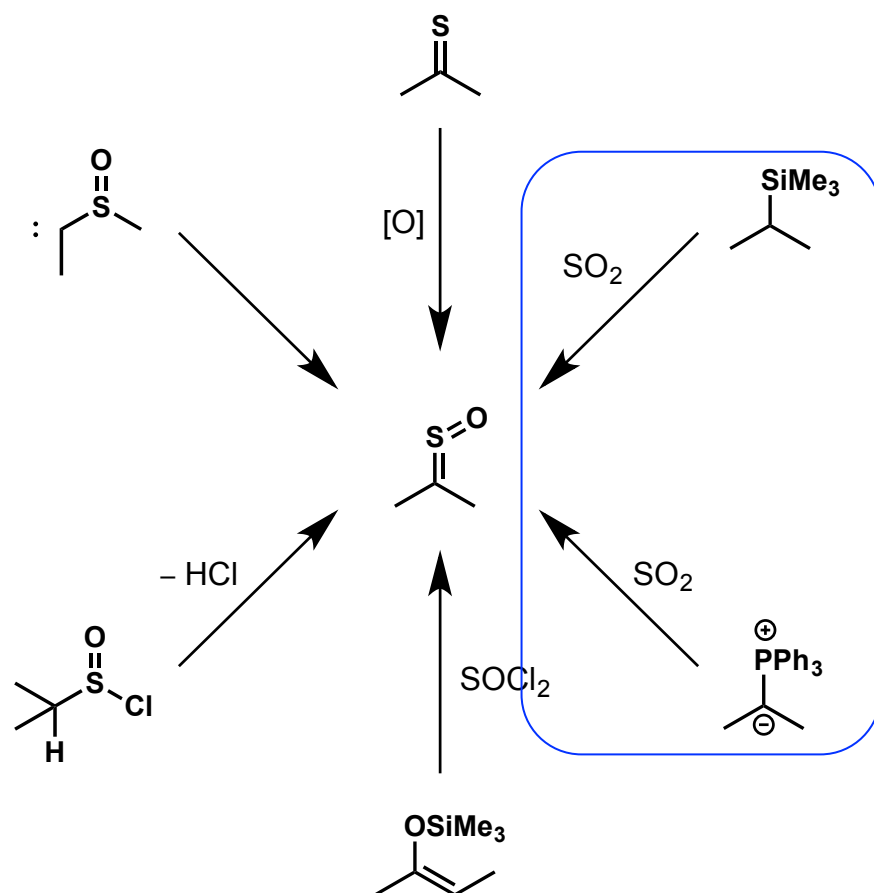
Preparation of Sulfines – Sulfenylation



Faull, A. W.; Hull, R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1078.

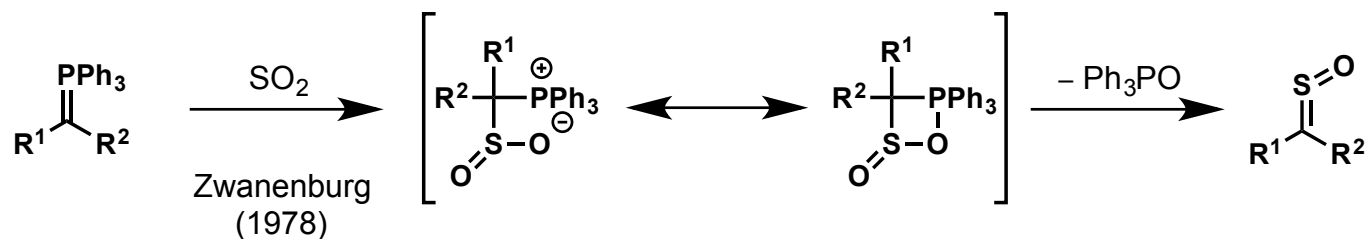
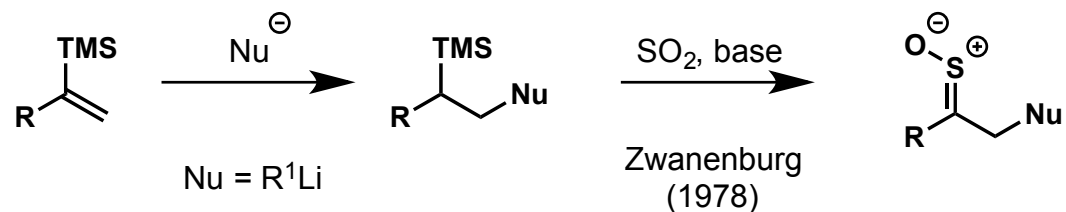
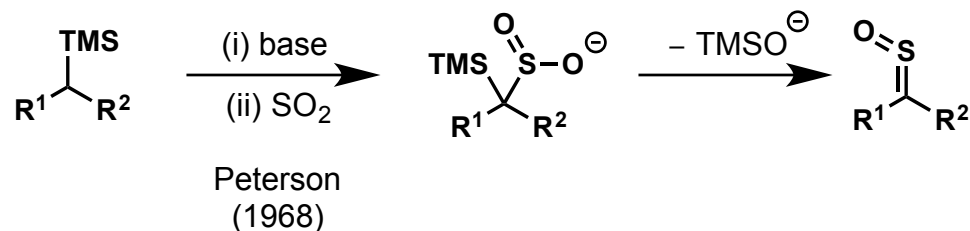
Lenz, B. G.; Regeling, H.; Van Rozendaal, H. L. M.; Zwanenburg, B. *J. Org. Chem.* **1985**, 50, 2930.

Preparation of Sulfines – Alkylidenation



- α-silyl carbanions proceed via α-silyl sulfinates
- Phosphonium ylides proceed via sulfobetaines

Preparation of Sulfines – Alkylidenation

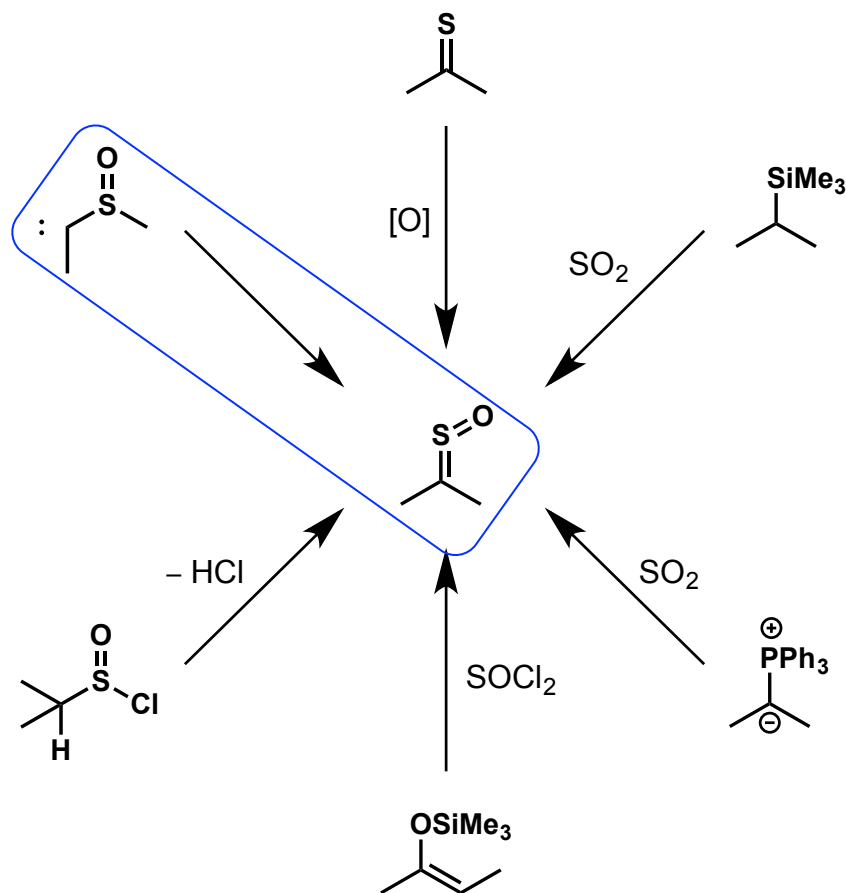


Peterson, D. J. *J. Org. Chem.* **1968**, 33, 780.

van der Leij, M.; Zwanenburg, B. *Tetrahedron Lett.* **1978**, 19, 3383.

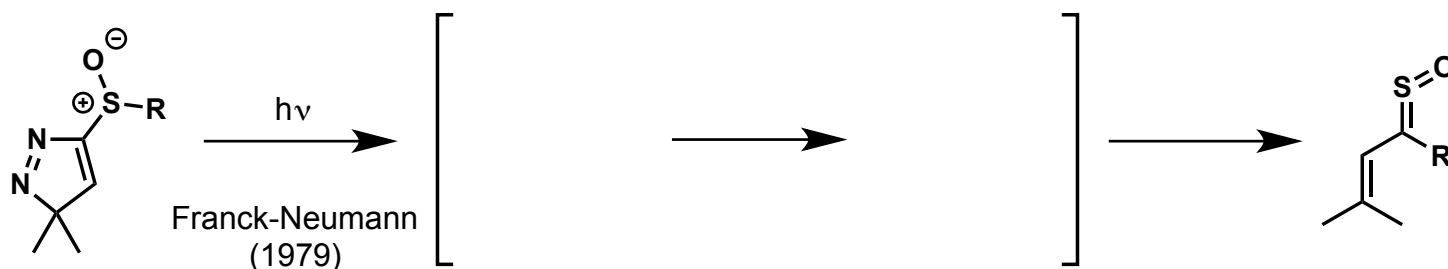
Zwanenburg, B.; Venier, C. G.; Porskamp, P. A. T. W.; van der Leij, M. *Tetrahedron Lett.* **1978**, 19, 807.

Preparation of Sulfoxes – Rearrangement



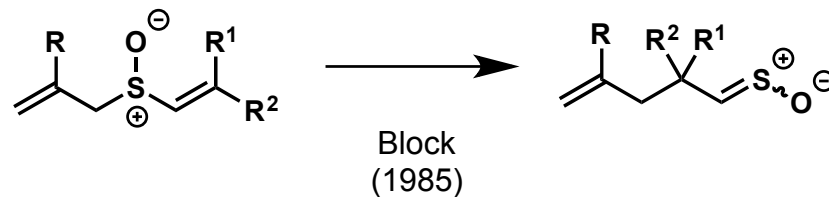
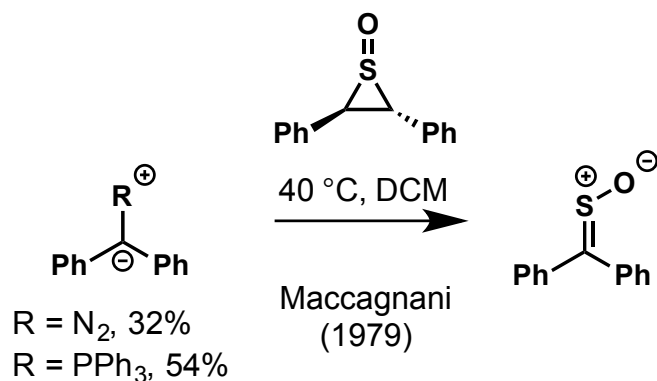
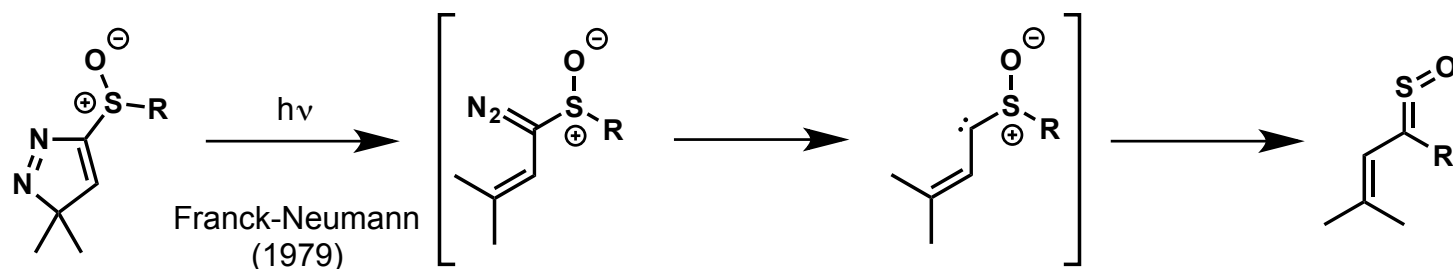
- Sulfoxides are easily oxidized from sulfides, which are prevalent
- Involve:
 - Carbenes
 - Sigmatropic Rearrangements
 - Radicals

Preparation of Sulfines – Rearrangement



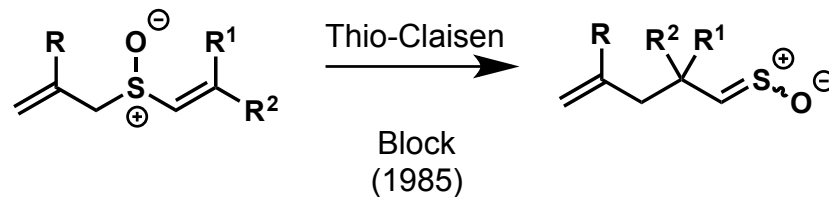
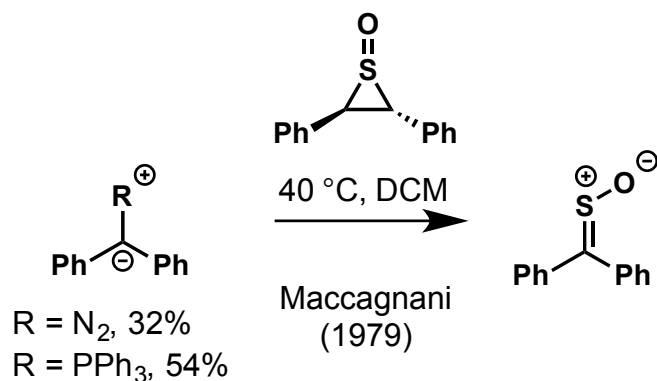
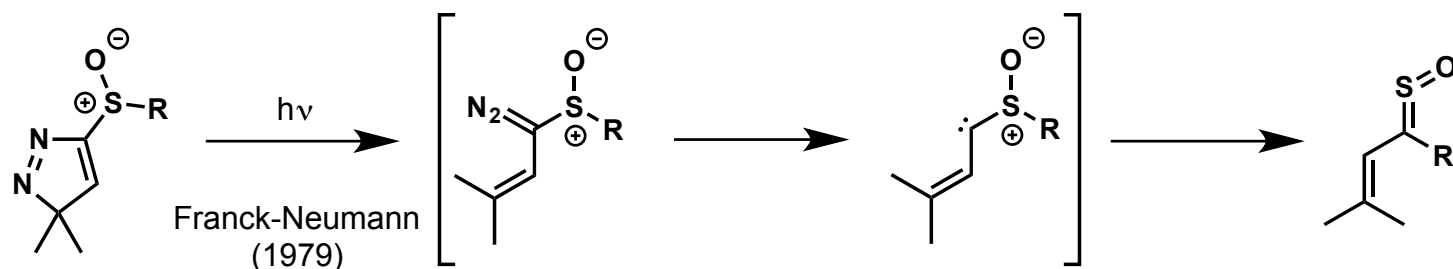
Franck-Neumann, M.; Lohmann, J. J. *Tetrahedron Lett.* **1979**, 20, 2397.
Bonini, B. F.; Maccagnani, G.; Mazzanti, G. *J. Chem. Soc., Chem. Commun.* **1976**, 431.
Block, E.; Ahmad, S. *J. Am. Chem. Soc.* **1985**, 107, 6731.

Preparation of Sulfines – Rearrangement



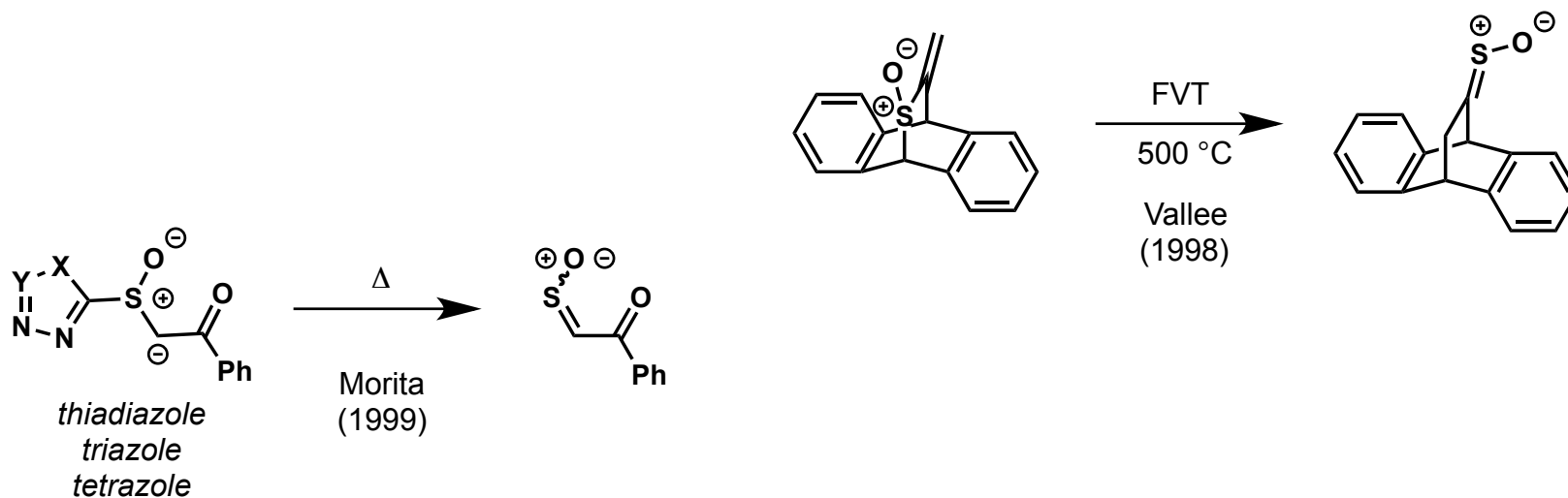
Franck-Neumann, M.; Lohmann, J. J. *Tetrahedron Lett.* **1979**, 20, 2397.
 Bonini, B. F.; Maccagnani, G.; Mazzanti, G. *J. Chem. Soc., Chem. Commun.* **1976**, 431.
 Block, E.; Ahmad, S. *J. Am. Chem. Soc.* **1985**, 107, 6731.

Preparation of Sulfines – Rearrangement

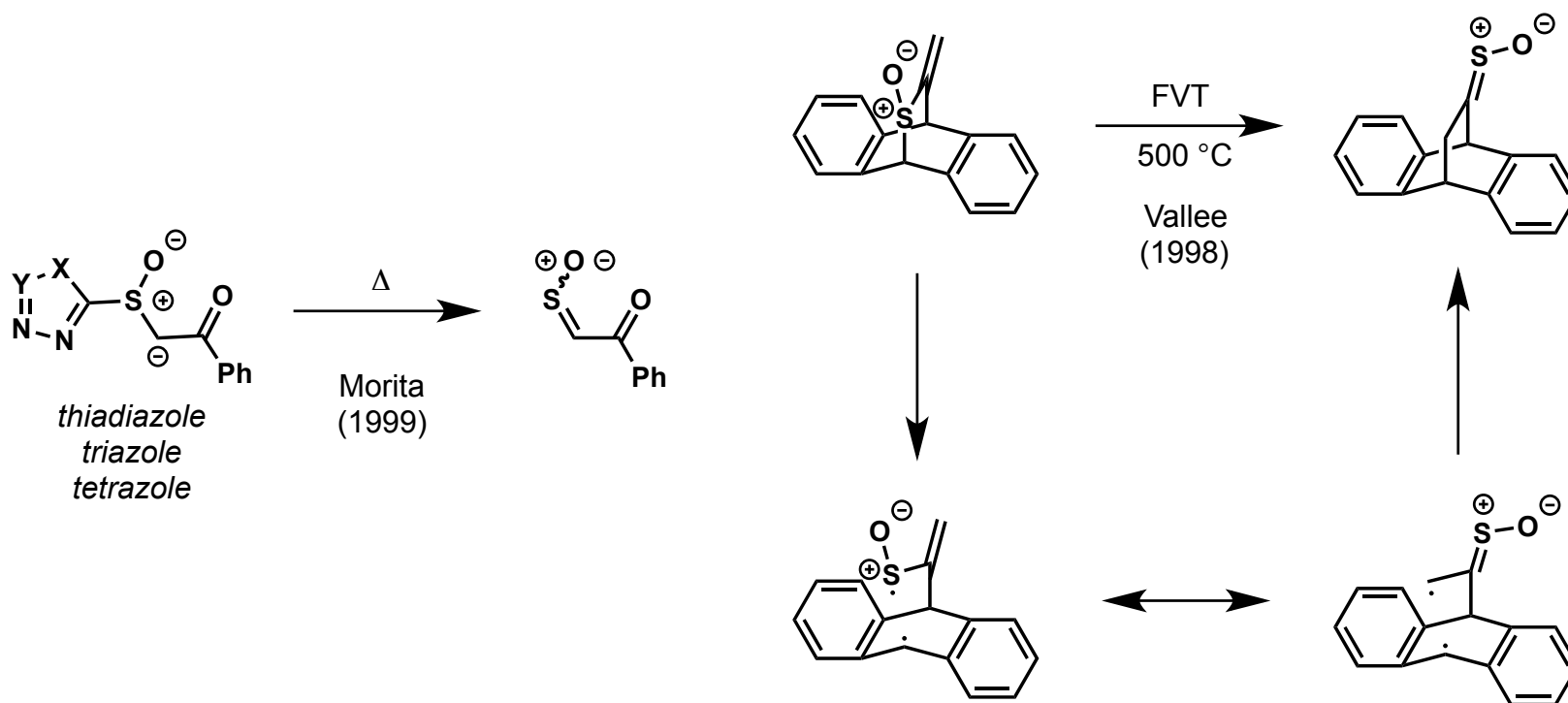


Franck-Neumann, M.; Lohmann, J. J. *Tetrahedron Lett.* **1979**, 20, 2397.
 Bonini, B. F.; Maccagnani, G.; Mazzanti, G. *J. Chem. Soc., Chem. Commun.* **1976**, 431.
 Block, E.; Ahmad, S. *J. Am. Chem. Soc.* **1985**, 107, 6731.

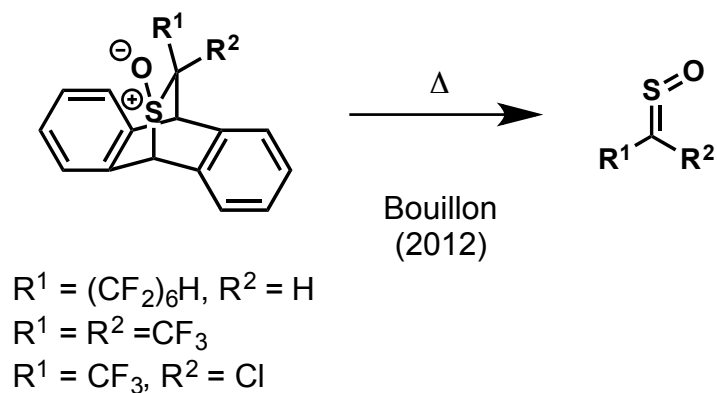
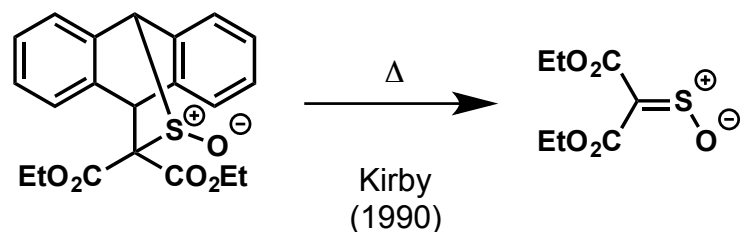
Preparation of Sulfines – Rearrangement



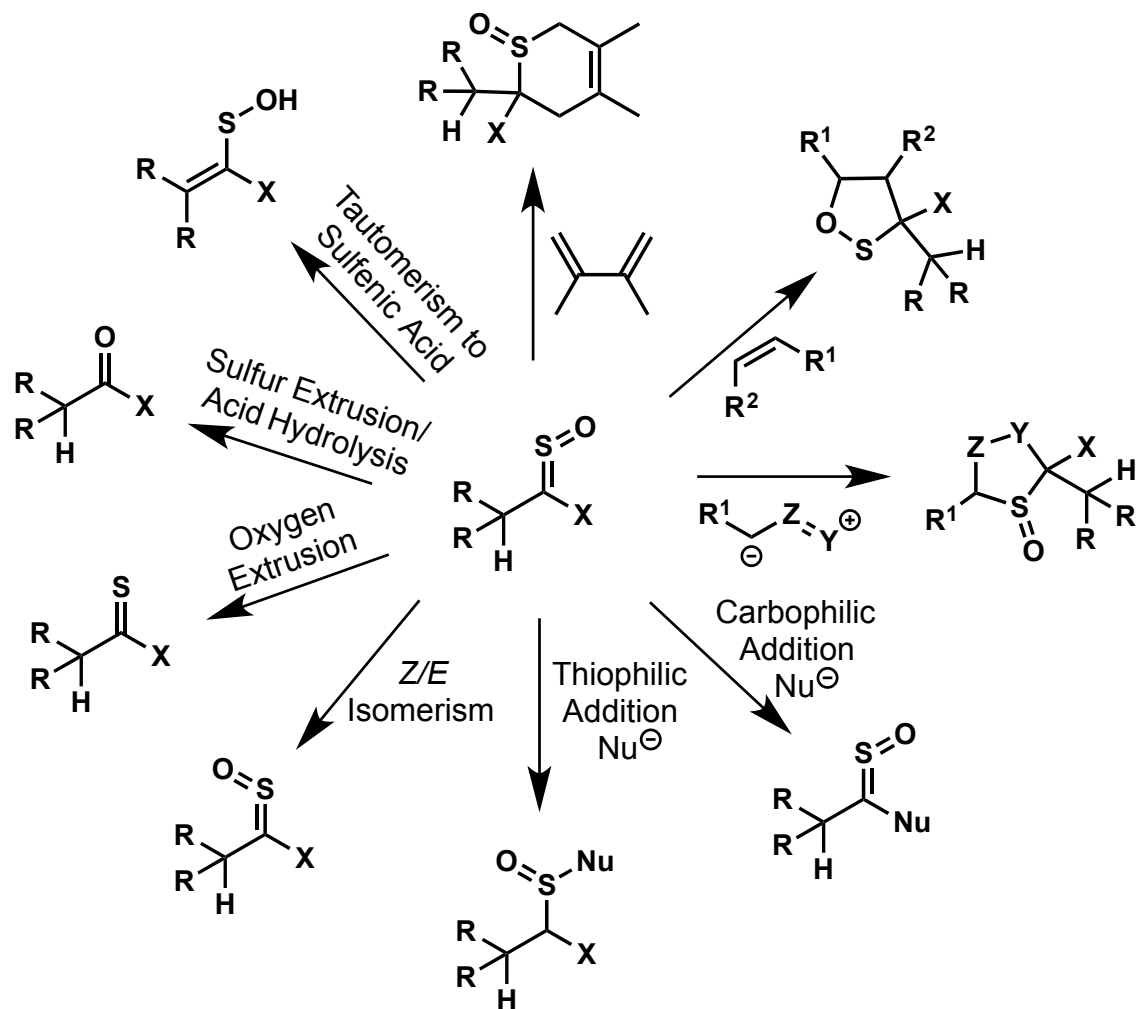
Preparation of Sulfines – Rearrangement



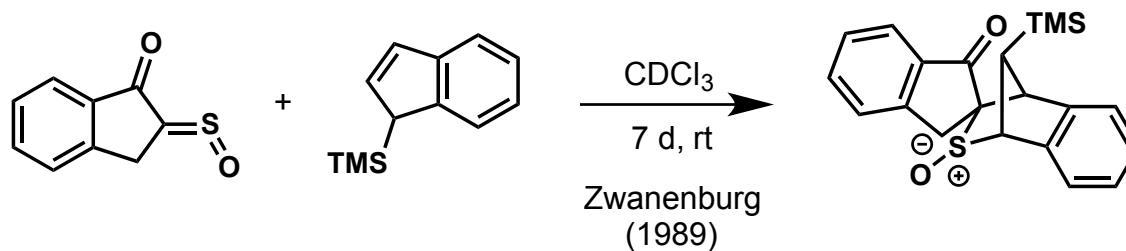
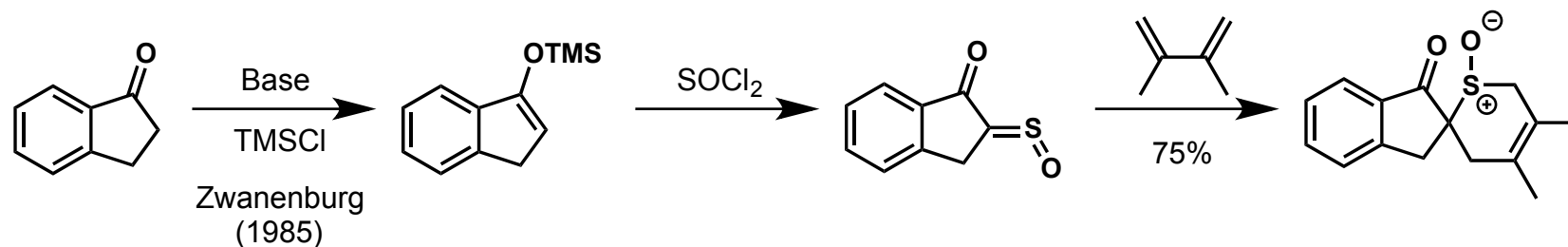
Preparation of Sulfines – Retro-Diels–Alder



Reactions of Sulfines



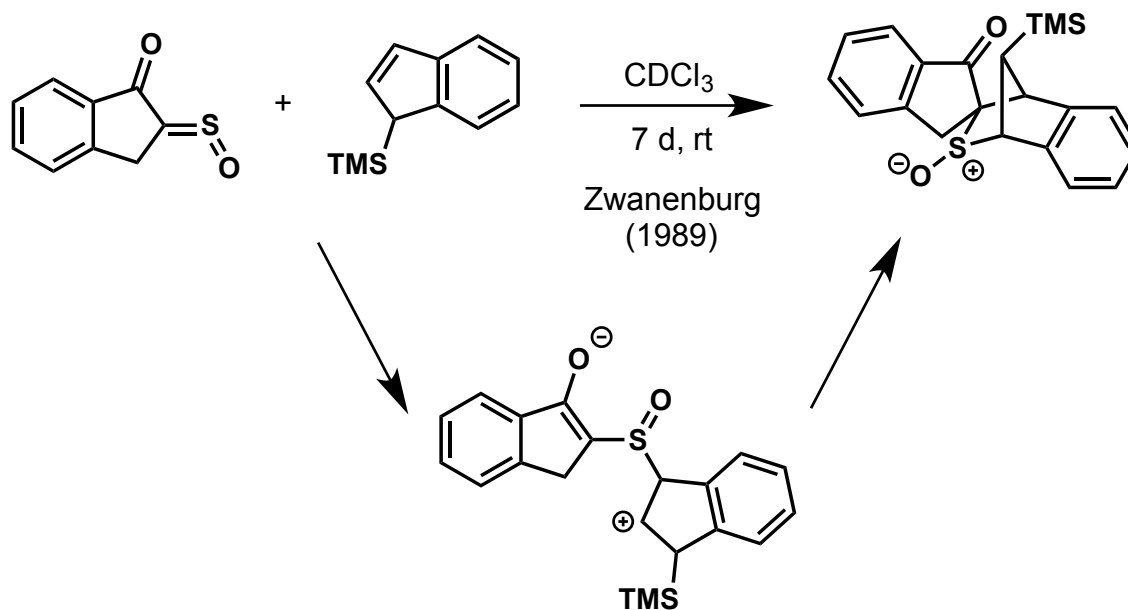
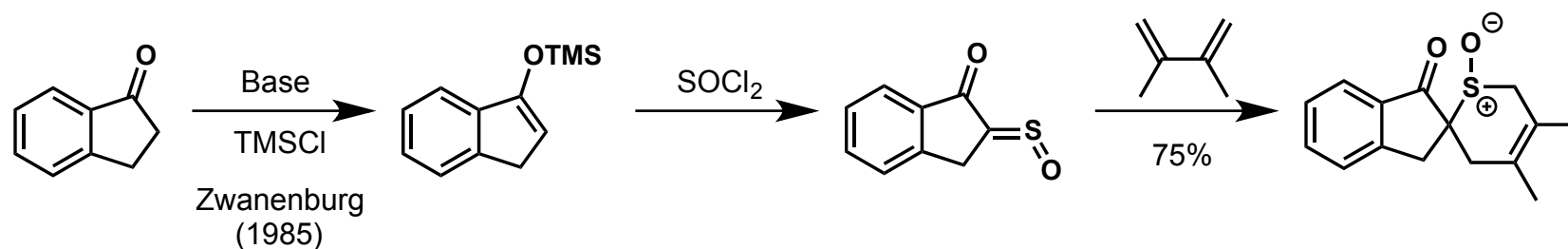
Reactions of Sulfines – Diels–Alder



Lenz, B. G.; Regeling, H.; Van Rozendaal, H. L. M.; Zwanenburg, B. *J. Org. Chem.* **1985**, *50*, 2930.

Rewinkel, J. B. M.; Zwanenburg, B.; García-Granda, S.; Beurskens, P. T.; Raaijmakers, R. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 61.

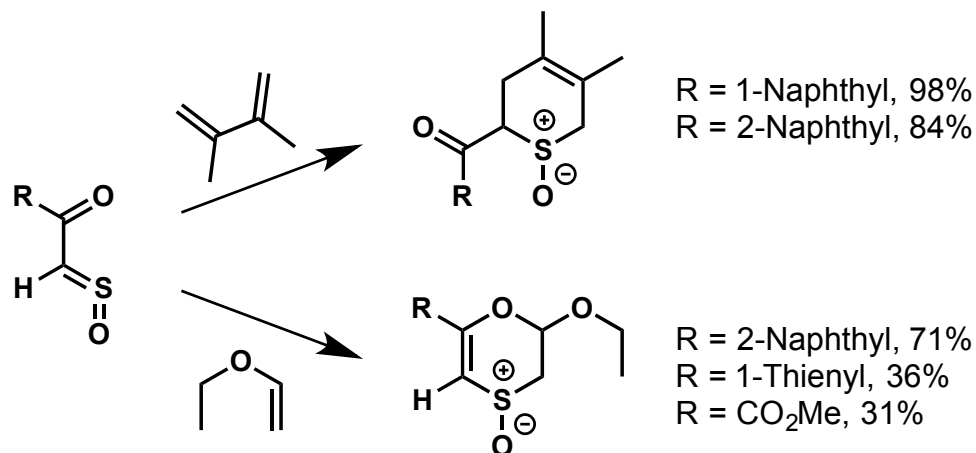
Reactions of Sulfines – Diels–Alder



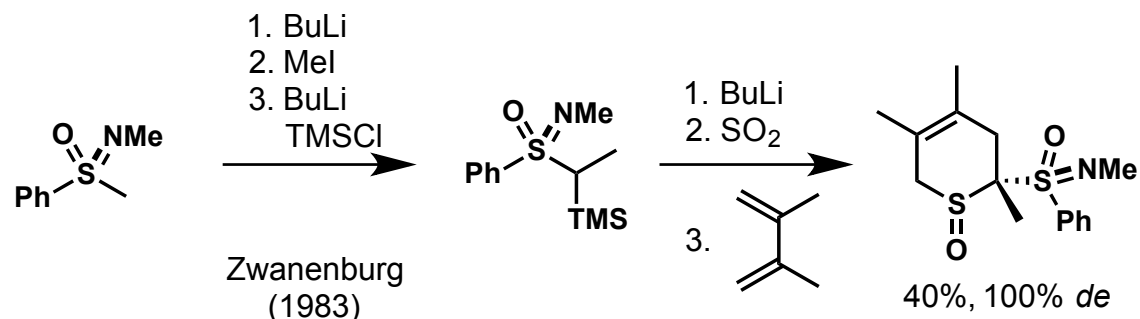
Lenz, B. G.; Regeling, H.; Van Rozendaal, H. L. M.; Zwanenburg, B. *J. Org. Chem.* **1985**, *50*, 2930.

Rewinkel, J. B. M.; Zwanenburg, B.; García-Granda, S.; Beurskens, P. T.; Raaijmakers, R. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 61.

Reactions of Sulfines – Diels–Alder



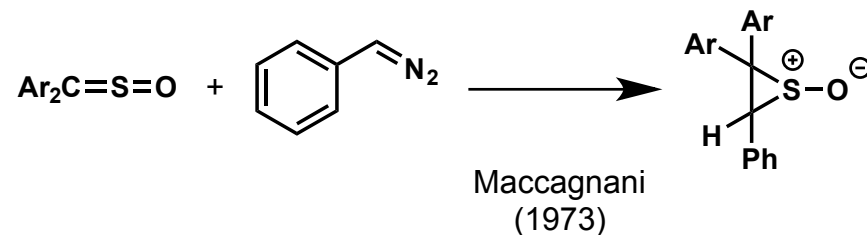
Capozzi
(1997)



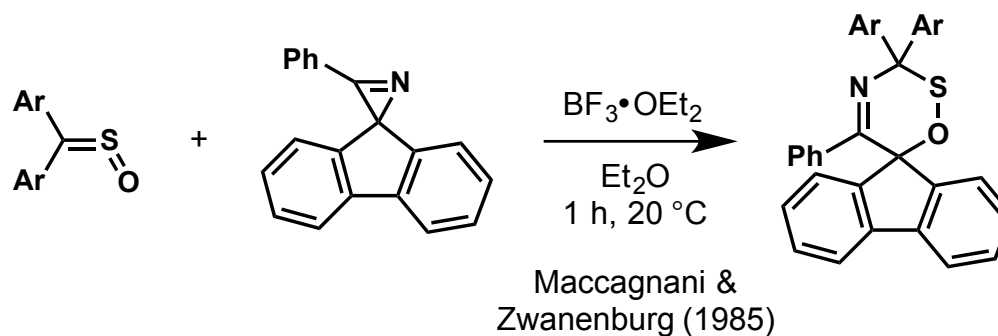
Capozzi, G.; Corti, A.; Menichetti, S.; Nativi, C. *Tetrahedron Lett.* **1997**, 38, 5041.

Porskamp, P. A. T. W.; van der Leij, M.; Lammerink, B. H. M.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1983**, 102, 400.

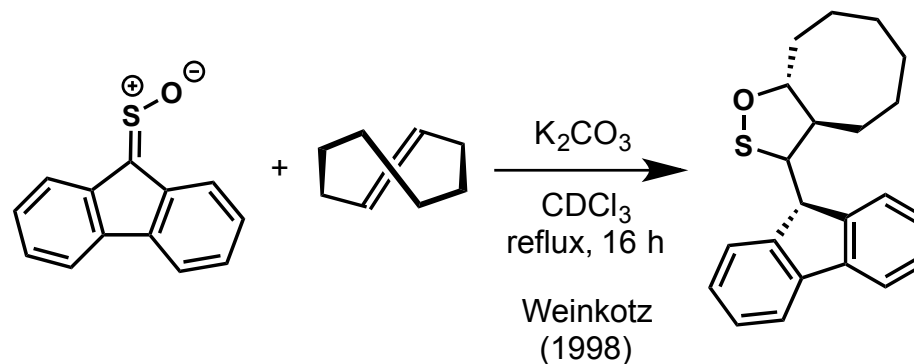
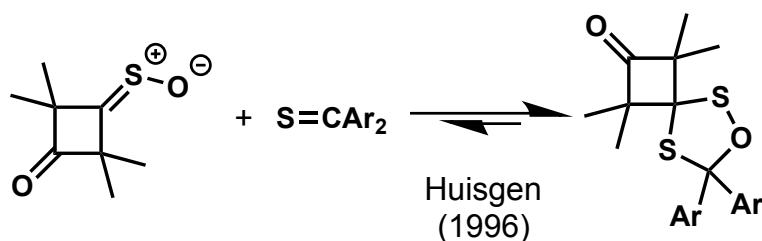
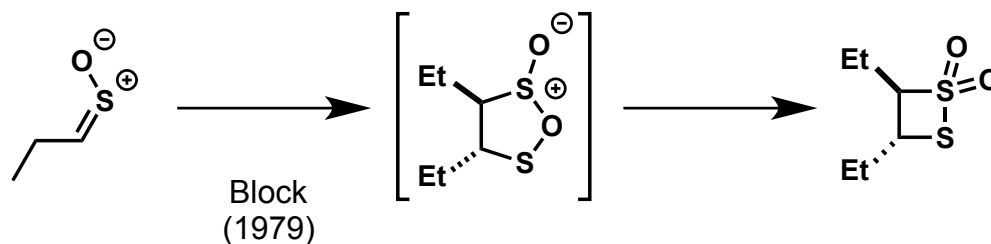
Reactions of Sulfines – [1+2]



Reactions of Sulfines – [3+3]

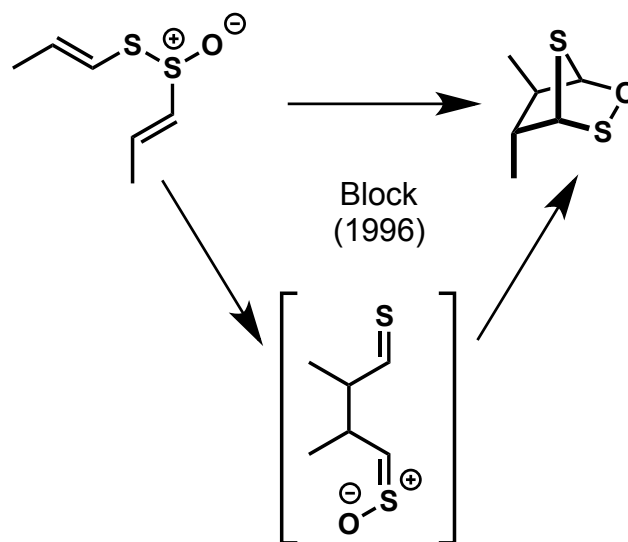
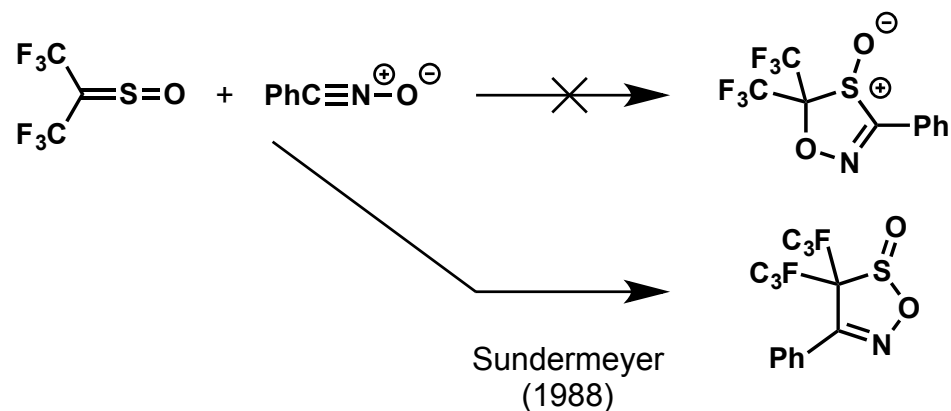


Reactions of Sulfines – 1,3-Dipolar



Block, E.; Penn, R. E.; Reville, L. K. *J. Am. Chem. Soc.* **1979**, *101*, 2200.
 Huisgen, R.; Molston, G.; Polborn, K. *J. Org. Chem.* **1996**, *61*, 6570.
 Adam, W.; Weinkotz, S. *J. Am. Chem. Soc.* **1998**, *120*, 4861.

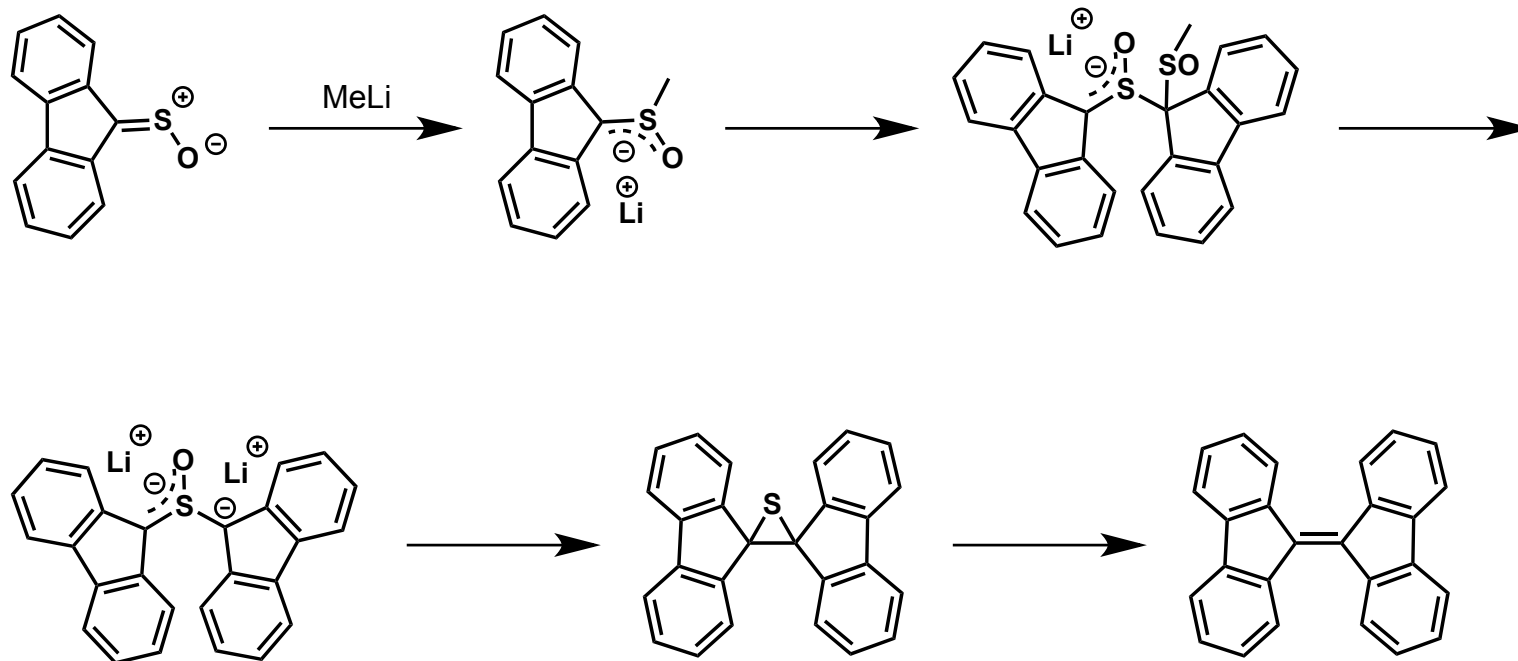
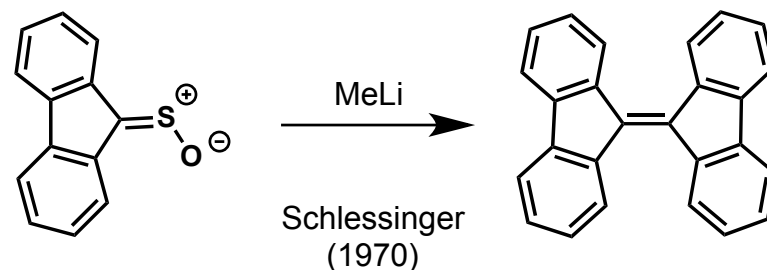
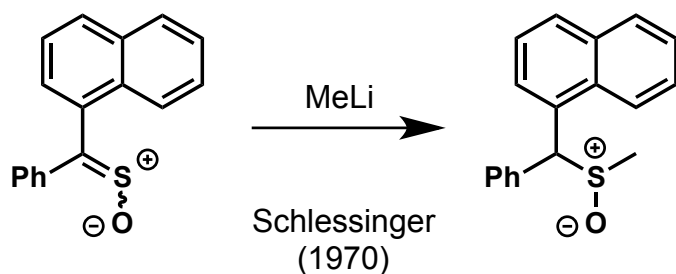
Reactions of Sulfines – 1,3-Dipolar



Schwab, M.; Sundermeyer, W. *Chem. Ber.* **1988**, 121, 75.

Block, E.; Thiruvazhi, M.; Toscano, P. J.; Bayer, T.; Grisoni, S.; Zhao, S.-H. *J. Am. Chem. Soc.* **1996**, 118, 2790.

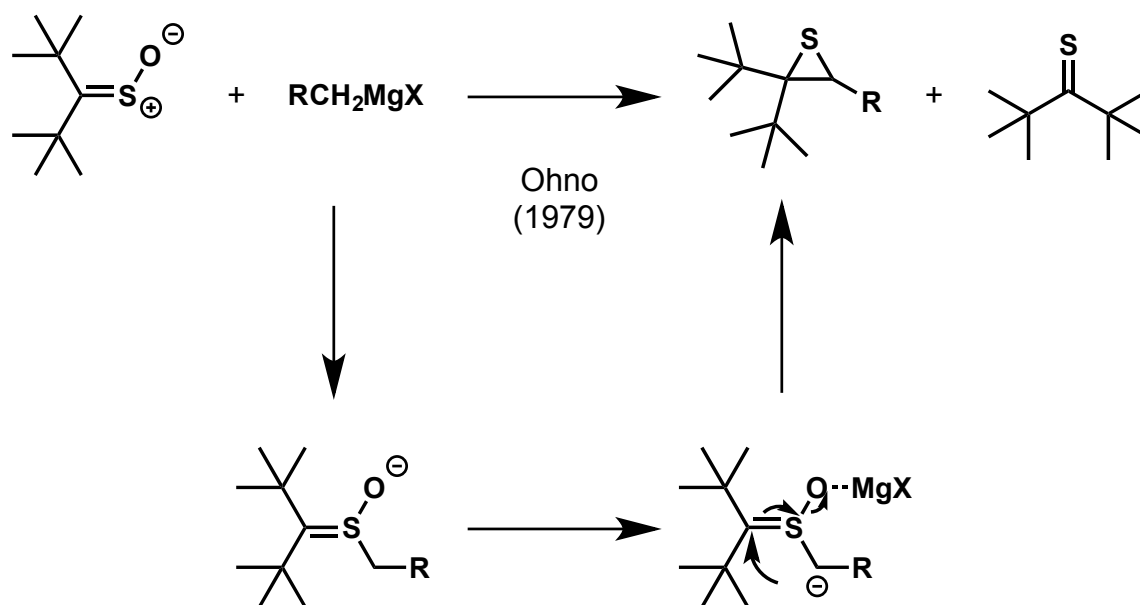
Reactions of Sulfines – Thiophilic Attack



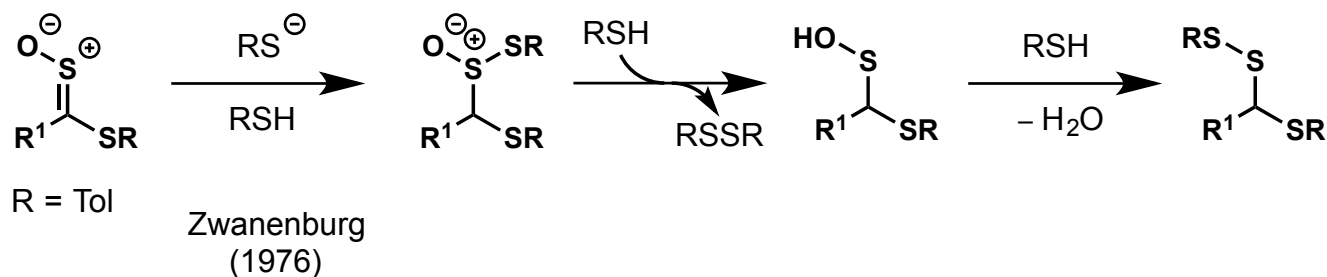
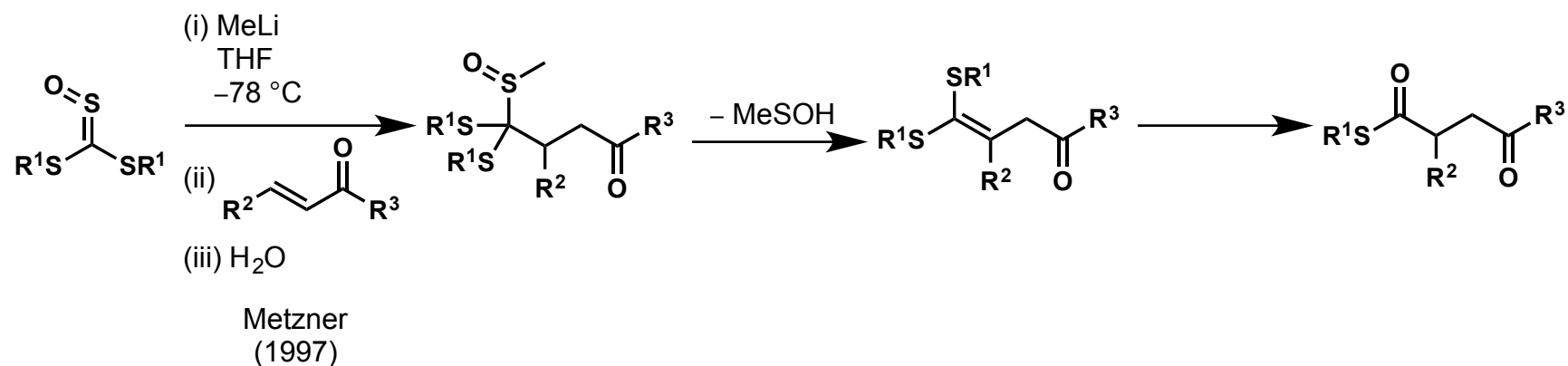
Schultz, A. G.; Schlessinger, R. H. *J. Chem. Soc. D* **1970**, 747.

Schultz, A. G.; Schlessinger, R. H. *J. Chem. Soc. D* **1970**, 748.

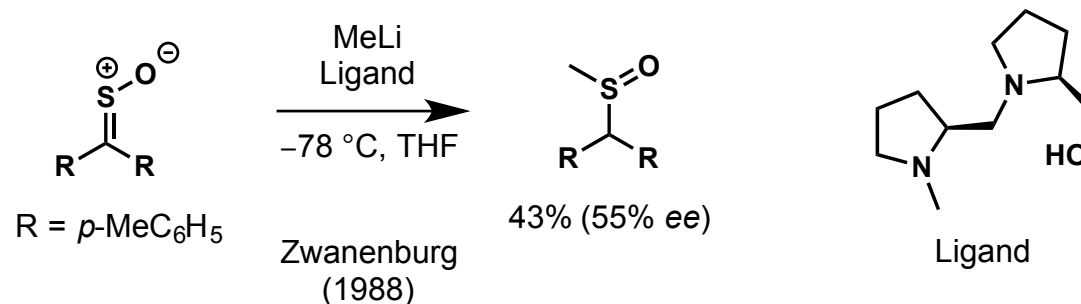
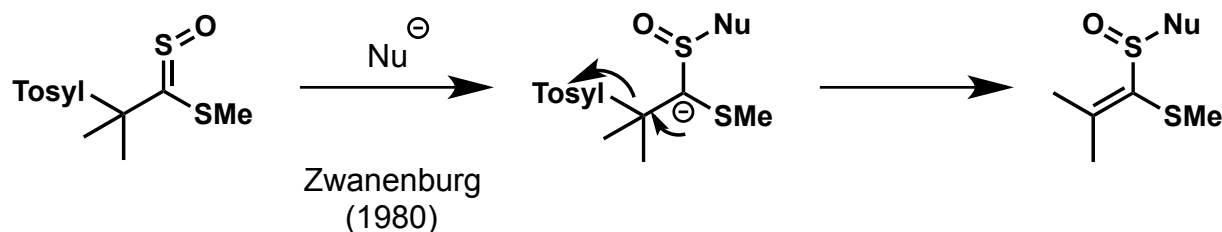
Reactions of Sulfines – Thiophilic Attack



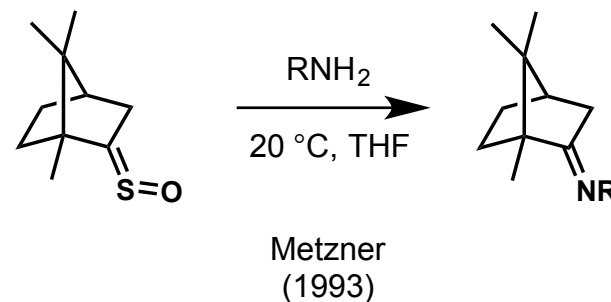
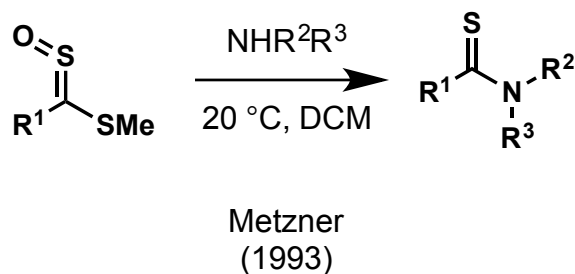
Reactions of Sulfines – Thiophilic Attack



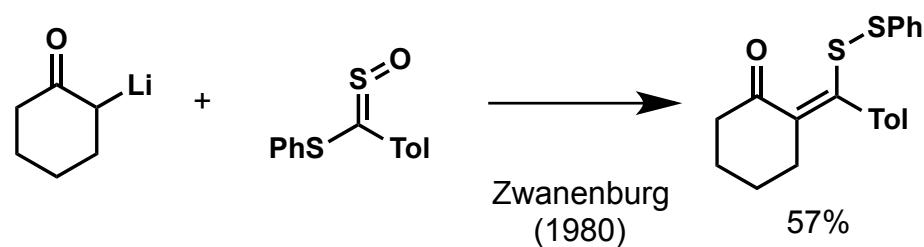
Reactions of Sulfines – Thiophilic Attack



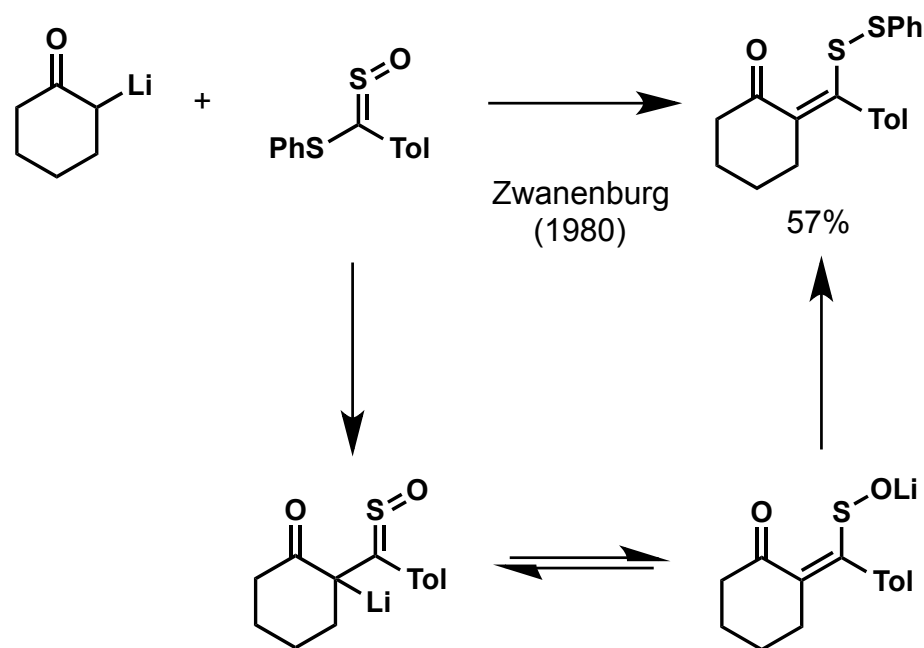
Reactions of Sulfines – Carbophilic Attack



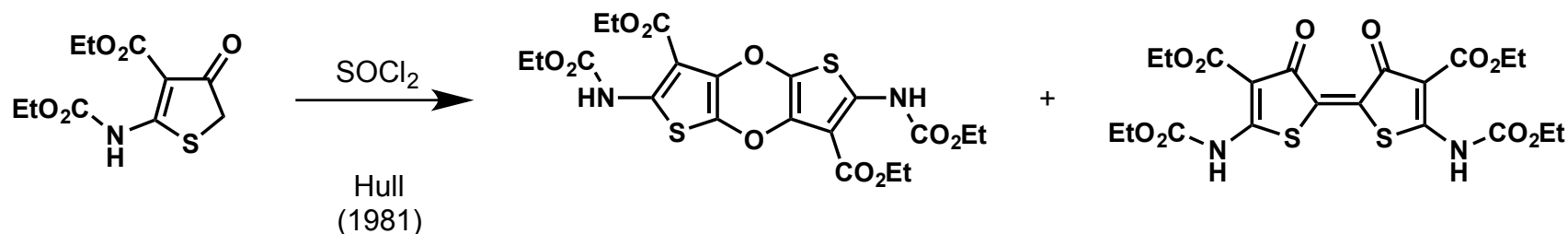
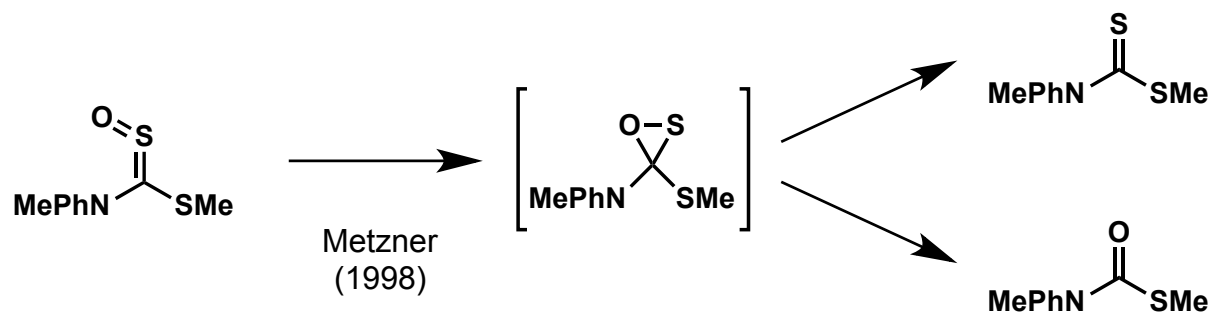
Reactions of Sulfines – Carbophilic Attack



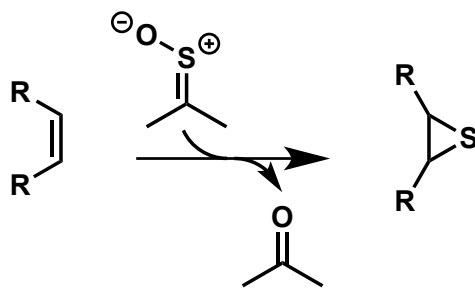
Reactions of Sulfines – Carbophilic Attack



Reactions of Sulfines – Rearrangements

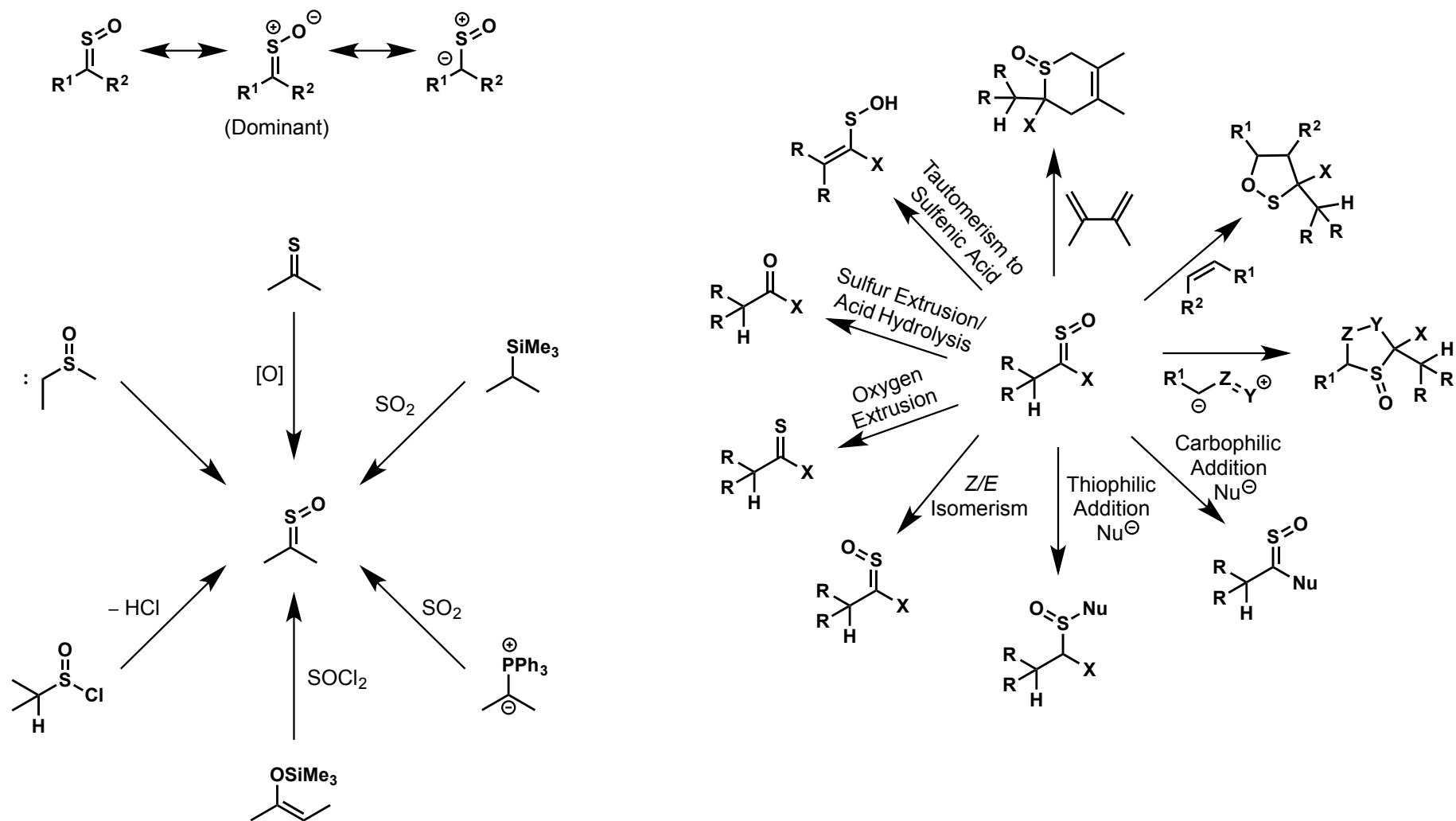


Reactions of Sulfines – Sulfur Transfer



Weinkötz
(1997)

Summary



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