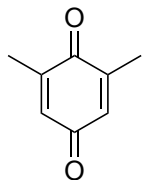


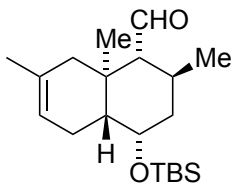
Enantioselective Total Synthesis of the Diterpenes Kempene-2, Kempene-1, and 3-epi-Kempene-1 from the Defense Secretion of Higher Termites

Melanie Schubert and Peter Metz

Angew. Chem. Int. Ed. **2011**, *50*, 2954

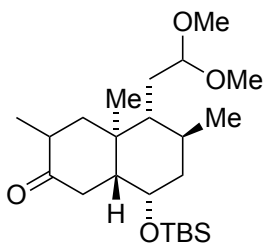


1-11



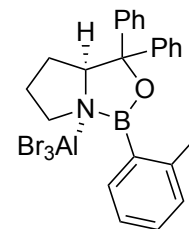
A

1-11



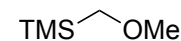
B

- 1) **1** (5 mol%), 2-methyl butadiene
- 2) Zn, AcOH, reflux (remember acid+heat)
- 3) L-selectride, THF
- 4) MOMCl, DIPEA, DCM
- 5) i. **2**, *s*-BuLi, THF $-60\text{ }^{\circ}\text{C}$ to $-23\text{ }^{\circ}\text{C}$
ii. **substrate**, $-78\text{ }^{\circ}\text{C}$ to $-60\text{ }^{\circ}\text{C}$
iii. KH $-60\text{ }^{\circ}\text{C}$ to r.t.
- 6) TFA, DCM, r.t.
- 7) **3**, LiHMDS, THF, $0\text{ }^{\circ}\text{C}$ *then* substrate
- 8) *p*-TsOH, MeOH, reflux
(deprotection also occurs)
- 9) TBSOTf, 2,6-lutidine, DCM, $0\text{ }^{\circ}\text{C}$
- 10) $\text{BH}_3\cdot\text{SMe}_2$, THF, *then* $\text{H}_2\text{O}_2/\text{KOH}$
- 11) Dess-Martin periodinane, DCM
 $0\text{ }^{\circ}\text{C}$ to r.t.



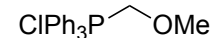
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- 1) Name Reaction?
- 2) Who developed this catalyst?



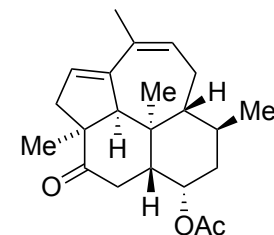
2

- 5) Name Reaction?
- Mechanism?

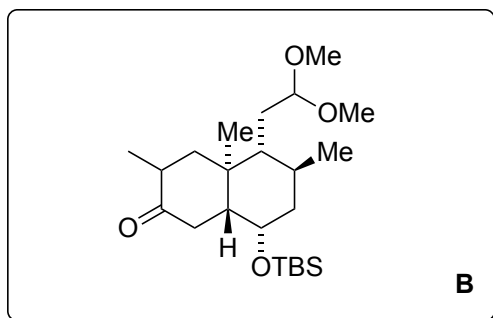


3

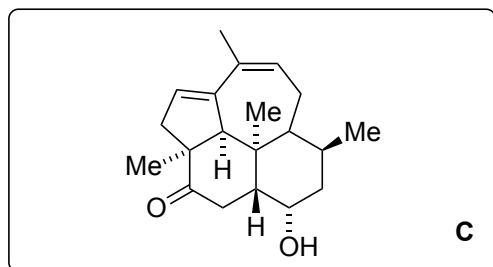
- 11) Structure of Dess-Martin? How to make?



(+)-kempene-2

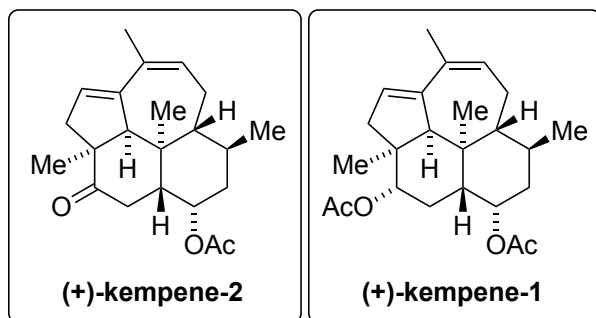


12-20



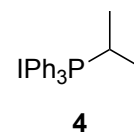
21

22-23

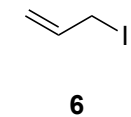
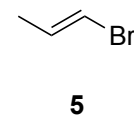


- 12) TMSI, HMDS, THF, r.t.
- 13) DDQ, benzene, r.t.
- 14) PPTS, acetone, reflux
- 15) **4**, *n*-BuLi, THF, 0 °C *then* **substrate**
- 16) **5**, *n*-BuLi, THF -78 °C *then* Me₃Al *then* **substrate**, TBSOTf
- 17) 2N HCl, THF, r.t.
(selective deprotection)
- 18) MeLi, 0 °C, *then* HMPA, **6**, -20 °C
(side product formed, what is it?)
- 18b) **side product**, toluene, reflux
- 19) 5 mol% Grubbs GII, DCM, reflux
- 20) TBAF, THF, reflux

- 21) Ac₂O, pyridine, DMAP
- 22) LiAlH₄, THF (2:1 d.r.)
- 23) Ac₂O, pyridine, DMAP



13) Mechanism?



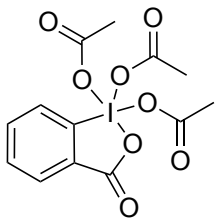
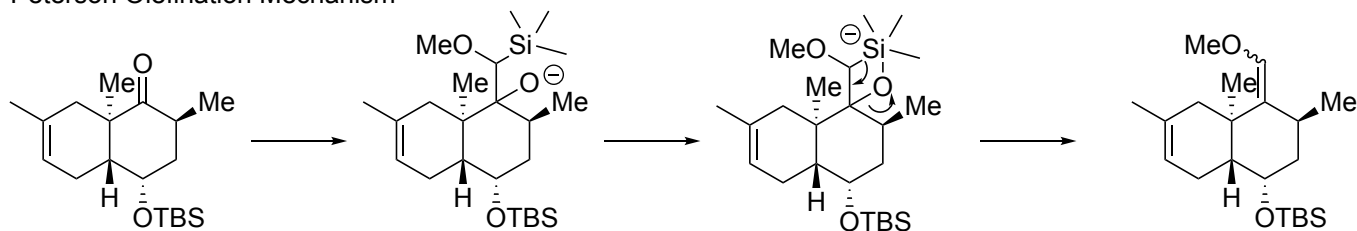
18) What is the Side Product

18b) Mechanism?

19) Name Reaction?
Mechanism? Catalyst
Structure?

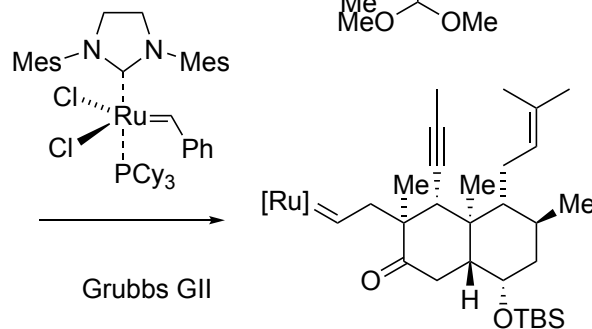
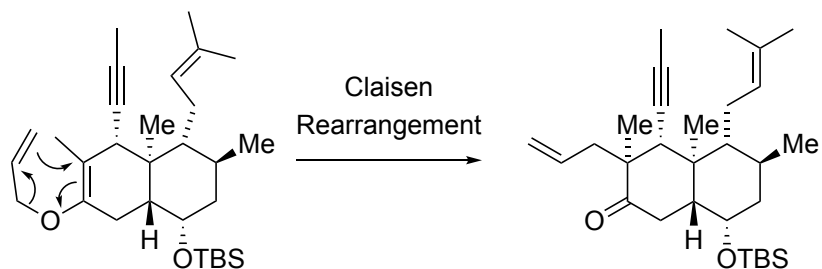
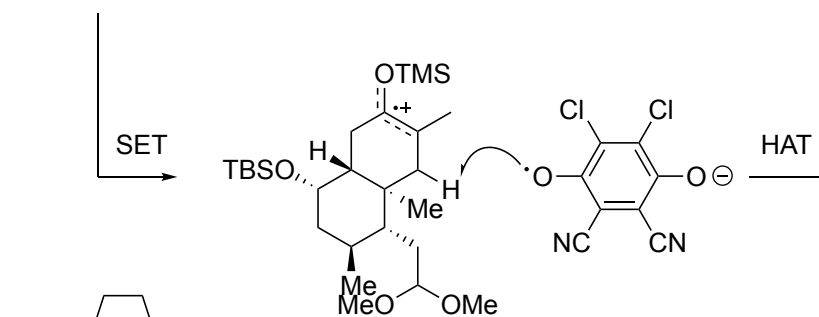
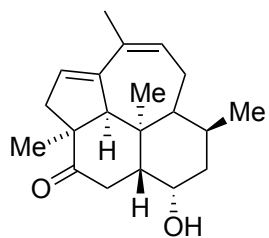
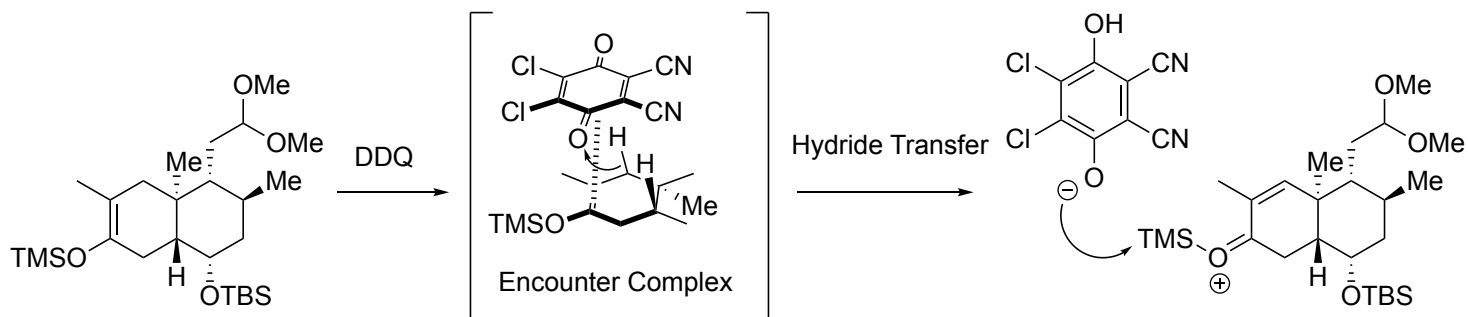
- 1) Name Reaction? - Diels-Alder
- 2) Who developed this catalyst? - E. J. Corey
- 5) Name Reaction? Mechanism? Peterson Olefination
- 11) Structure of Dess-Martin? *o*-iodobenzoic acid/Oxone then Ac_2O

Peterson Olefination Mechanism



Dess-Martin Periodinane

13) Mechanism?
 18) What is the Side Product
 18b) Mechanism?
 19) Name Reaction?
 Mechanism? Catalyst
 Structure?



O-alkylated side product

