14-Step Synthesis of (+)-Ingenol from (+)-3-Carene

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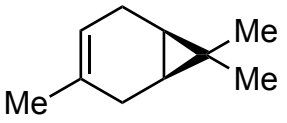
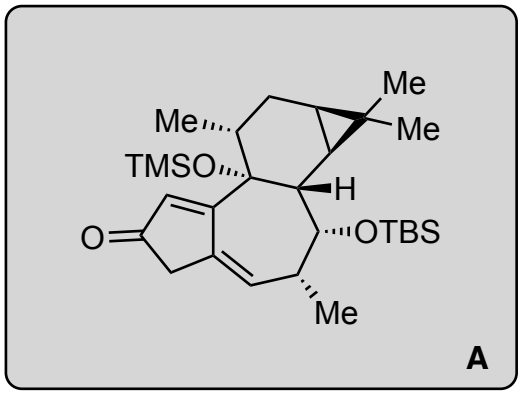
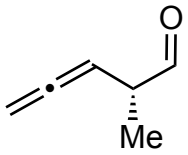


1-6



7-10

1) NCS, DMAP
2) O_3, thiourea
3) Lithium naphthalenide, HMPA, MeI *then* LiHMDS **1**
4) Ethynyl magnesium bromide
5) TBSOTf (1 equiv) *then* TMSOTf (1 equiv)
6) $[Rh(Cl(CO)_2]_2$, CO



1

7) MeMgBr
8) OsO_4
9) CDI
10) $BF_3 \bullet OEt_2$

2) Name of the reaction? Why would you use thiourea? What other sulfur compound could you use? Please show the mechanism

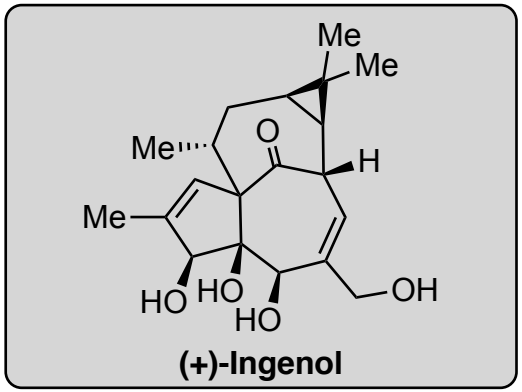
Ozonolysis;
Alternative: dimethylsulfide volatile and smelly, thiourea nonvolatile nonsmelly; mech below

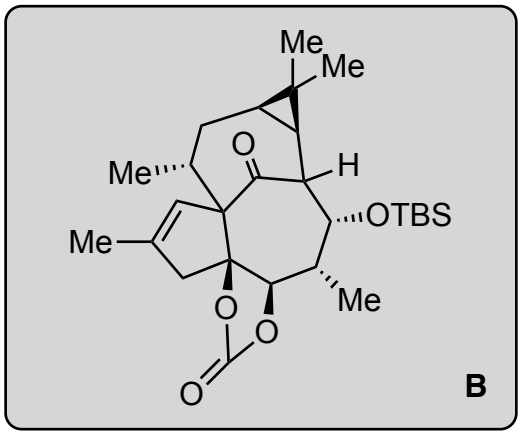
6) Name of the Reaction?

Pauson Khand
https://doi.org/10.1021/ol025955w

10) Name of the reaction?

vinylogous pinacol rerrangement



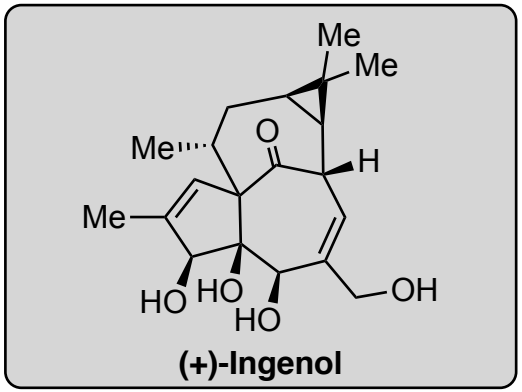


B

11-14

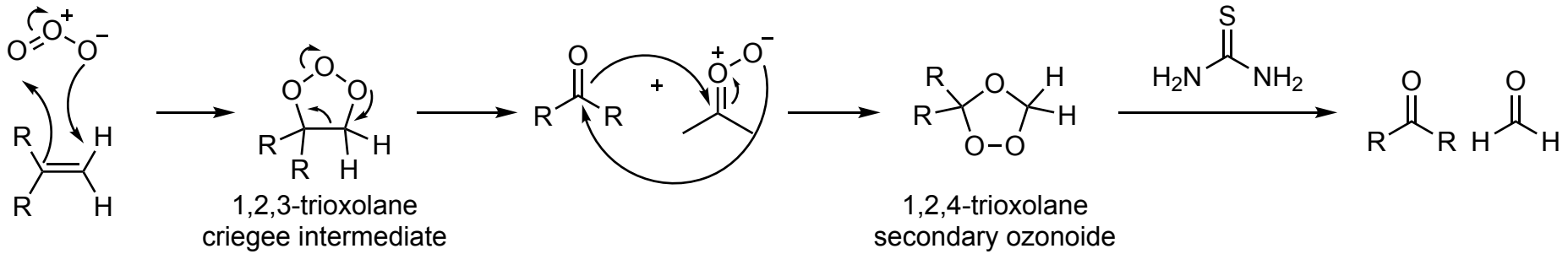
11) SeO_2 *then* Ac_2O
12) HF
13) Martin's Sulfurane *then* NaOH
14)SeO_2, HCO_2H

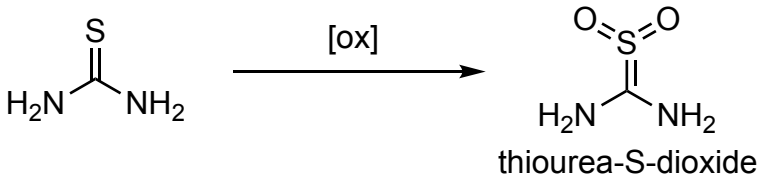
14) Name of the reaction? Please provide a mechanism
Riley oxidation



(+)-Ingenol

Ozonolysis:
Thiourea: https://doi.org/10.1016/0040-4020(82)80187-7
Criegee mechanism: https://www.organic-chemistry.org/namedreactions/ozonolysis-criegee-mechanism.shtm





Riley oxidation: