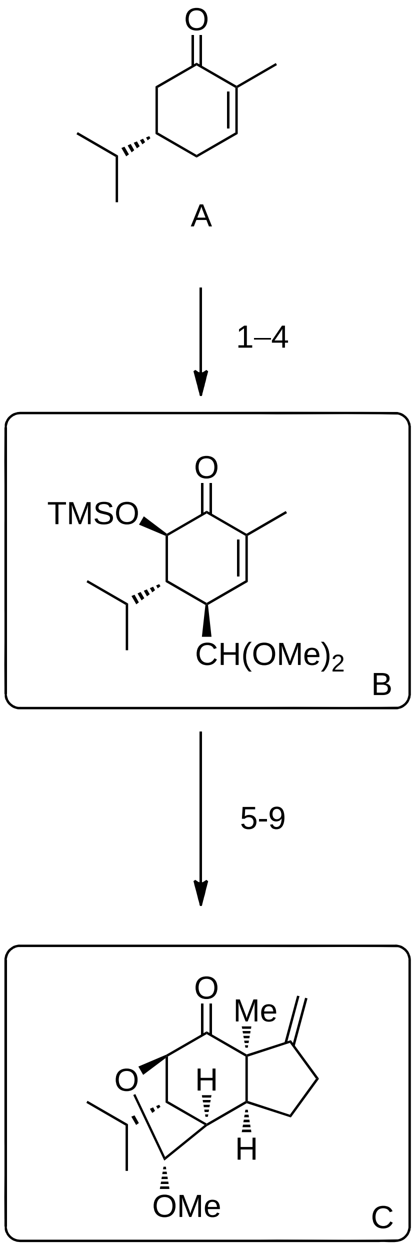
Total Synthesis of (–) Dendrobine via α-Carbonyl Radical Cyclization

Sha, C. K.; Chiu, R. T.; Yang, C. F.; Yao, N. T.; Tseng, W. H.; Liao, F. L.; Wang, S. L .

J. Am. Chem. Soc. **1997**, *119*, 4130–4135.



1) MeMgCl, $FeCl_3$, TMSCl, Et_3N
2) $CH(OMe)_3$, BF_3•OEt_2
3) LDA, TMSCl
4) *m*-CPBA, $NaHCO_3$

Hint: No 1,2 or 1,4 addition happened in step 1

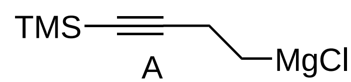
Name of step 3 and 4.

Provide another alternative method for this transformation.

Rubottom Oxidation

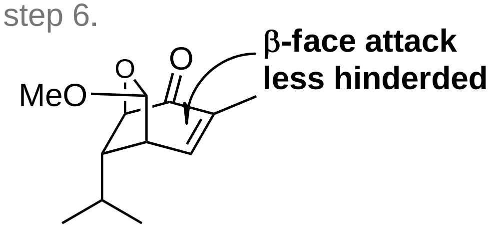
Davis Oxaziridine

5) PTSA, $CHCl_3$
6) CuI, **A**, then TMSCl, Et_3N
7) NaI, *m*-CPBA, THF
8) Bu_3SnH, AIBN, PhH
9) TFA, PhH



A

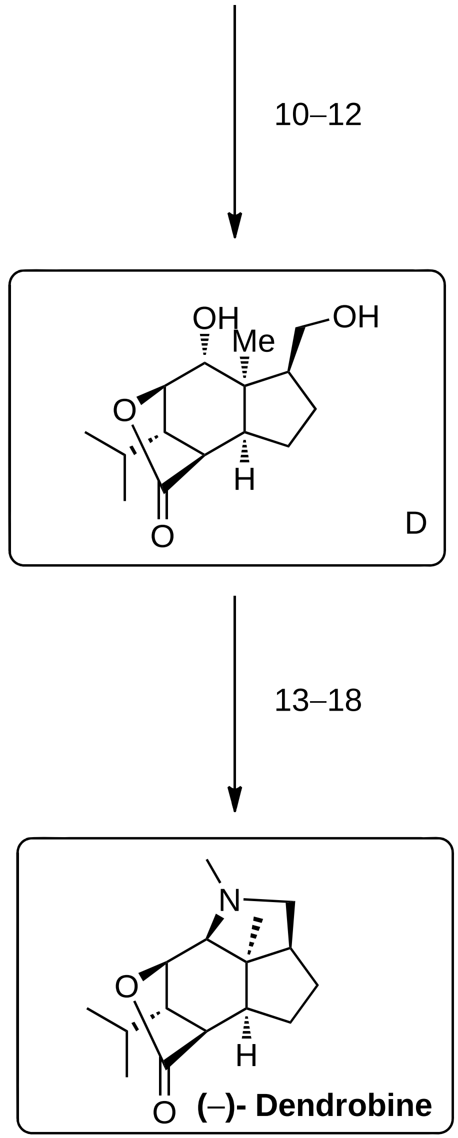
Explain the sterechemistry outcome of step 6.



For step 7, the author proposed an "I+" was generated from *m*-CPBA and NaI.

Sha, C.K. et.al. *J. Org. Chem*. **1987**, *52*, 3919-3920.

For a similar concept using $NaIO_4$/$NaHSO_3$ system, see, Shen, Z. et. al. *Tetrahedron. Lett*. **2014**, *55*, 1339-1341.



10) *m*-CPBA, BF_3•OEt_2, DCM
11) DBU
12) BH_3•SMe_2, then H_2O_2, NaOH

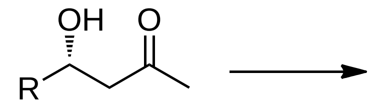
For step 10 and 11,
Related Reference:
One-step conversion of protected lactols to lactones
Grieco, P. A.; Oguri, T.; Yokoyama, Y. *Tetrahedron. Lett.* **1978**, *19*, 419-420.

13) MsCl, Et_3N
14) NaN_3, 18-Crown-6, DMF
15) CrO_3, H_2SO_4, H_2O, acetone
16) PPh_3, THF
17) $NaBH_3CN$, HOAc, MeOH
18) $(HCHO)n$, H_2O, HCO_2H

For the step 10 and 11, give the methanism of the related Kornblum-DeLaMare rearrangement

Provide a reaction mechanism of step 12.
Try to give the outcome of related name reactions.

(1) Evans-Saksena reduction
(2) Narasaka-Prasad reduction
(3) Evans-Tishchenko reaction



(4) Meerwein-Ponndorf-Verley reduction
(5) Cannizzaro reaction

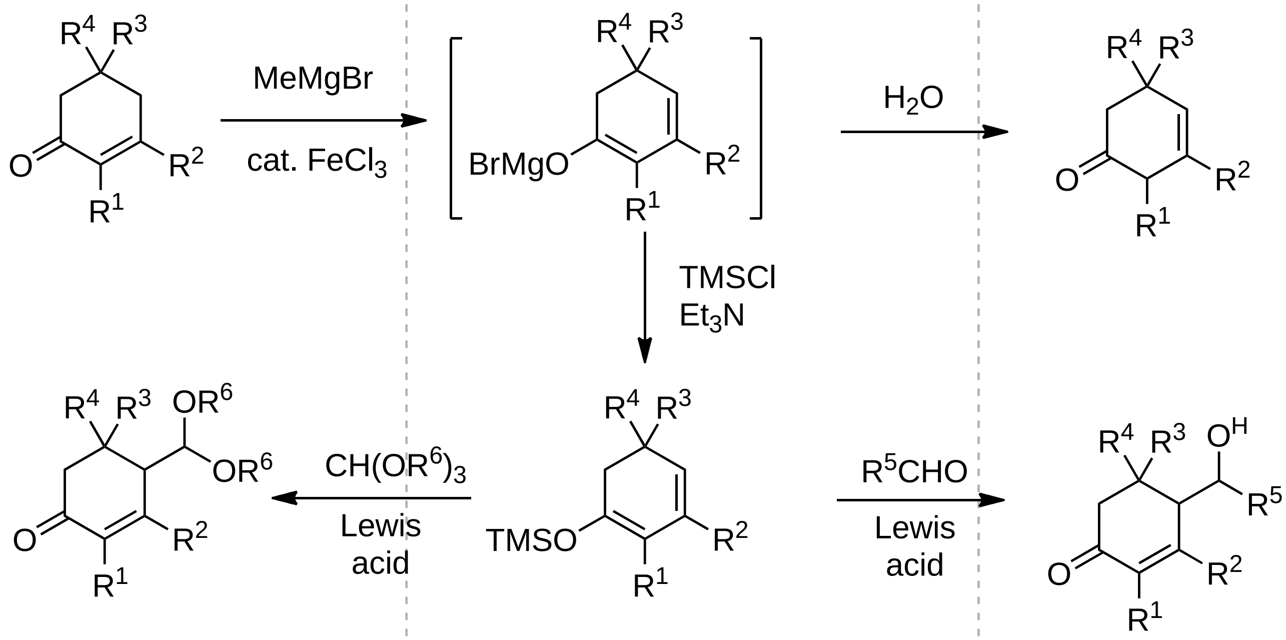
What the nucleophilicity parameter of azide in DMSO **20**

What name reaction is step 16 and formulate a reaction mechanism

Staudinger Reaction

Step 18
Eschweiler-Clarke reaction

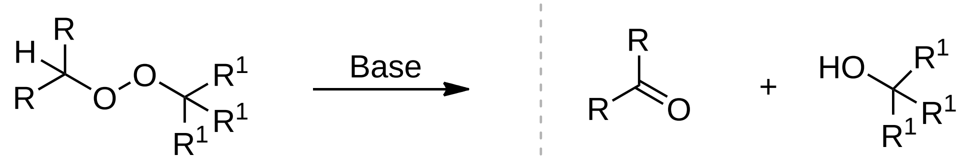
Step 1 and 2.



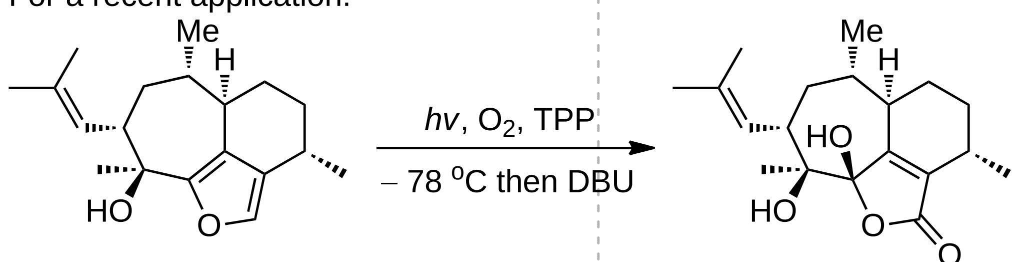
References: Kharasch, M. S.; Tawney, P. M. *J. Am. Chem. Soc.* **1941**, *63*, 2308-2316.
Takazawa, O.; et. al. *Bull. Chem. Soc, Jpn.* **1982**, *55*, 1907-1911.

Step 10 and 11.

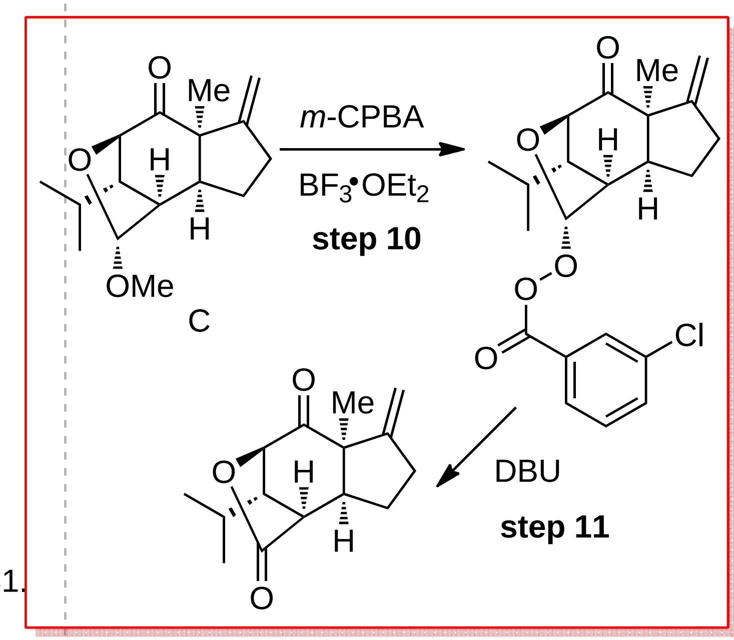
Kornblum-DeLaMare rearrangement:



For a recent application:

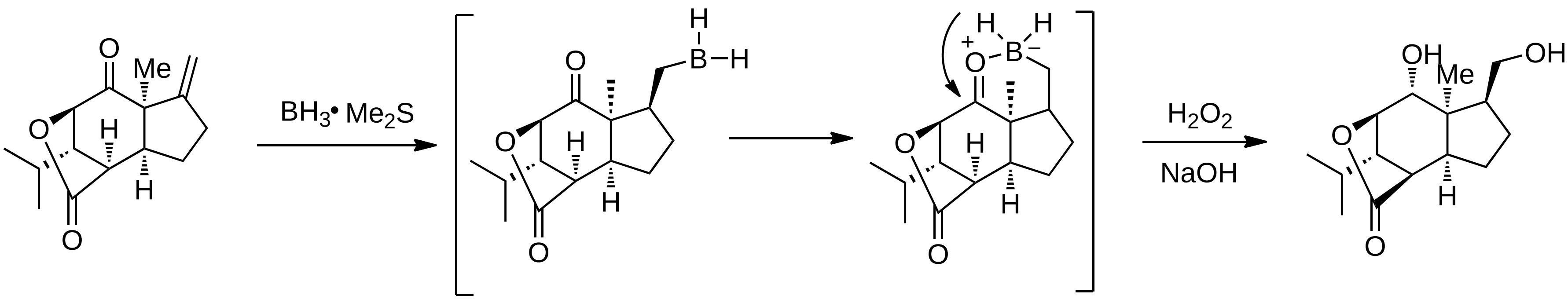


Sandresolide B

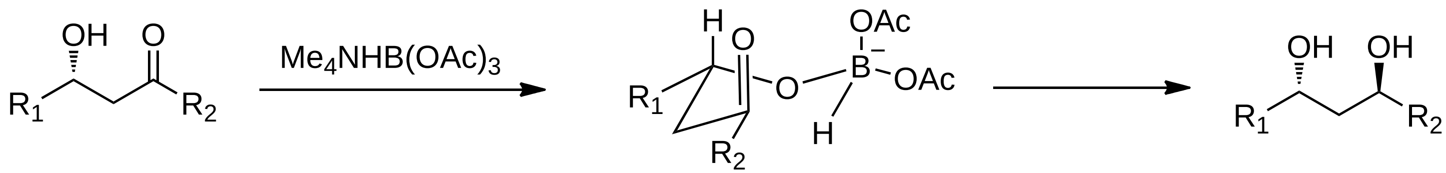


References: Kornblum, N.; DeLaMare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 880-881.
Trauner, D.; et. al. *Org. Lett.* **2014**, *16*, 166-169

Step 12.

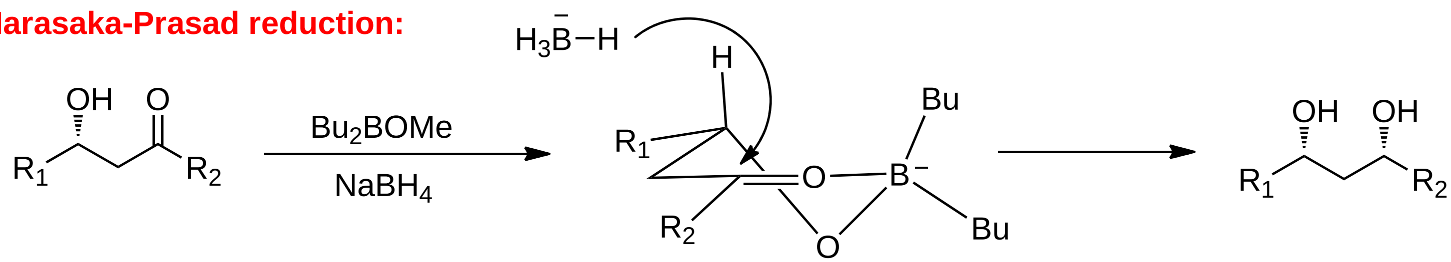


Evans-Saksena reduction:



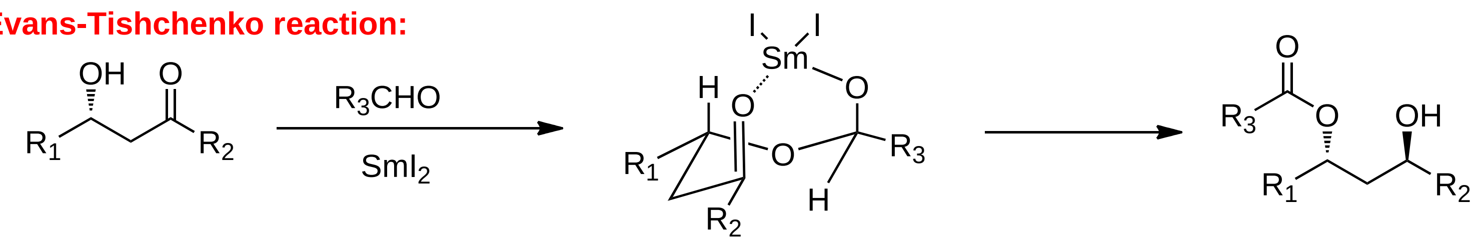
Saksena, A. K.; Mangiaracina, P. *Tetrahedron Lett.* **1983**, *24*, 273-276.
Evans, D. A.; Chapman, K.; Carreira. E. *J. Am. Chem. Soc.* **1988**, *110*, 3560-3578.

Narasaka-Prasad reduction:



Narasaka, K.; Pai, F. C. *Tetrahedron*. **1984**, *40*, 2233-2238.
Prasad, K. et. al. *Tetrahedron. Lett.* **1987**, *28*, 155-158.

Evans-Tishchenko reaction:



Evans, D.; Hoveyda, A. *J. Am. Chem. Soc*. **1990**, *112*, 6447-6449.

Staudinger Reaction Mechanism: