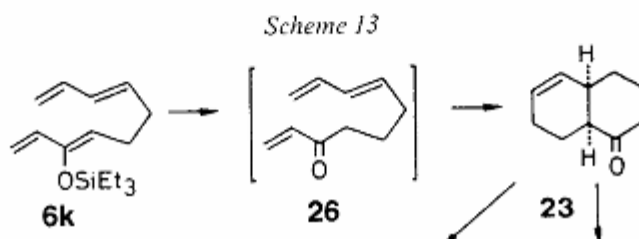


**Selected answers (with DOI where available):**

**1a.** from *Helv. Chim. Acta*, **1981**, 64(7), 2002

(Teacher's note: I spotted this reaction in a book on tandem reactions in the Reed library and I have assigned it to several classes, but I have never, until now, looked up the original reference. As the following shows, I gave you the wrong stereochemistry for the starting material. The starting material shown below gives the *cis*-fused product via an *endo* transition state. Interestingly, the authors also report a mistake; they had originally assigned the stereochemistry of **23** as *trans*.)

The alternative use of **4a** as an equivalent of **IV** in intramolecular *Diels-Alder* reactions was demonstrated by cleavage of the silyloxytetraene **6k** with KF in methanol at  $-10^{\circ}$  to  $0^{\circ}$  for 1 h. Subsequent work-up and chromatography furnished directly the *cis*-fused octahydronaphthalenone **23** as the sole adduct in 78% yield (*Scheme 13*). Evidently, the initially formed ketone **26** undergoes an exceedingly smooth and stereoselective intramolecular [4+2]-addition to the diene unit. The mild reaction conditions, coupled with the observation that no deuterium was found in **23** after cleavage of **6k** in  $\text{CD}_3\text{OD}$  are in accord with a kinetically controlled *Diels-Alder* process which favors an *endo*-orientation of the carbonyl group in the transition state<sup>5</sup>. This stereochemical assignment of the adduct **23** is opposite to our previous one [2] which was based on the hydrogenation of **23** with Pd/C in abs. EtOH leading to the *trans*-bicyclo[4.4.0]decan-2-one (**25**) (83%). The misleading epimerization which accompanies the hydrogenation **23**  $\rightarrow$  **25** could be avoided by hydrogenation of **23** using *Wilkinson's* catalyst [23] to give cleanly *cis*-bicyclo[4.4.0]decan-2-one (**24**), identified by comparison (GC.,  $^{13}\text{C}$ -NMR.) with an authentic sample prepared as described in [24]. Successive treatment of the cycloadduct **23** with  $\text{NaBH}_4$ ,  $\text{H}_2$ /Pd/EtOH and  $\text{CrO}_3$ /pyridine also furnished pure *cis*-**24**.



1b. from *Org Lett*, 2005, 7(4), 557-560, DOI 10.1021/ol047730m

### Scheme 2

