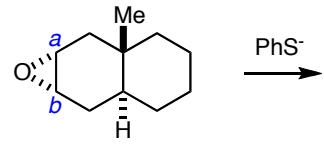
1 Epoxide **1** could, hypothetically, undergo ring opening via attack of the thiophenylate at the carbon marked *a* or that marked *b*. Draw chair conformations of the products **2** and **3**, respectively, and indicate which is more sable.



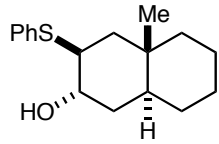
1

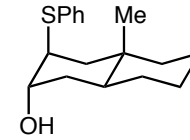
2 **3**

2

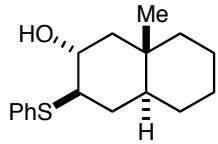
3

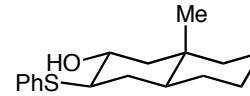
The decalin system locks the rings. Compound **2** has axial hydroxyl and thiophenyl groups so it is the least stable.





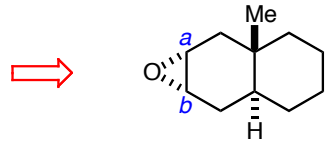
2
less stable





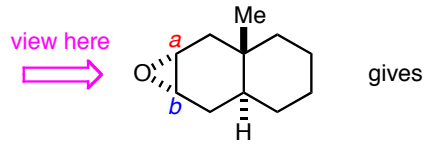
3
more stable

2 In the previous problem, the *less* stable product **2** is formed almost exclusively. Draw the starting material **1** in a chair form from the perspective shown (draw just the epoxide and the closest cyclohexane ring), and use the concept that the carbon attacked "rises" to nucleophiles as the addition occurs (it must to form a tetrahedral carbon) to draw conformations of the products **2** and **3** at the instant they form. This is to rationalize why the *least stable compound* **2** is *kinetically* preferred.

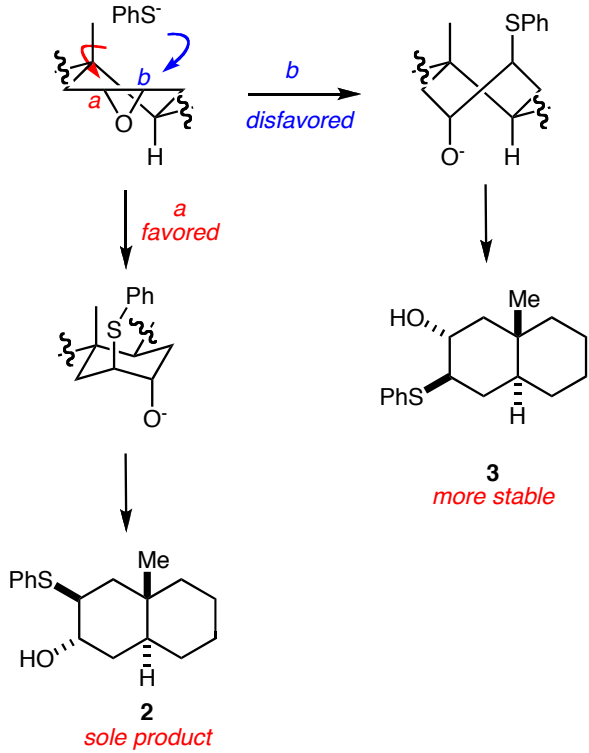


1

Attack via pathway a gives a chair form. Even though this has two new axial substituents it is still more stable than the twist boat formed via b (actually the transition states preceding the chair and twist boat intermediates are critical: Curtin Hammett).



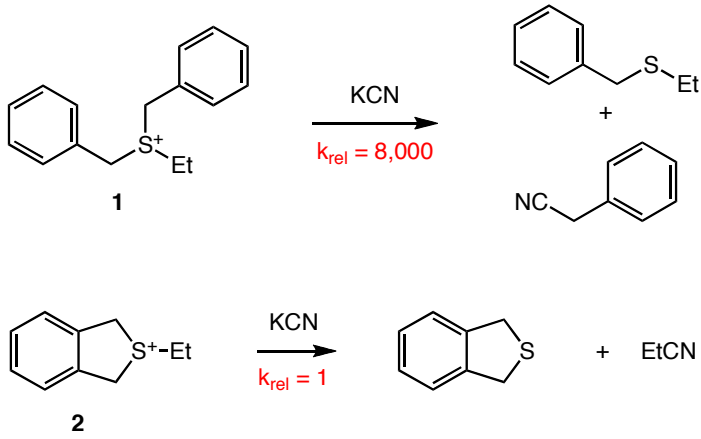
1



3
more stable

2
sole product

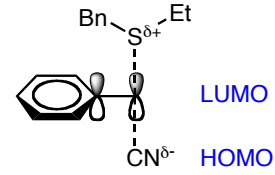
3 Explain the different rates and products observed for electrophiles **1** and **2** by considering reasons why S_N2 reactions are accelerated for benzylic electrophiles.



1

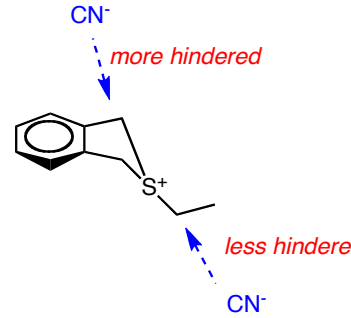
2

Phenyl substituents tend to accelerate S_N2 substitutions because the electrophile σ^*-orbital energy level (LUMO) is lowered via interaction with orbitals in the aromatic π-system. Substrate **1** reacts relatively fast for this reason. This type of interaction is precluded for **2** so the sterically more accessible ethyl group is attacked.



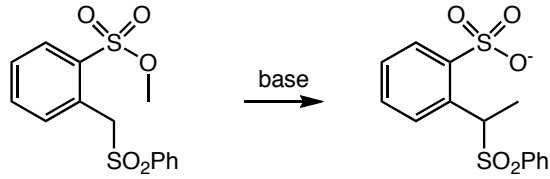
transition state stabilized

from **1**



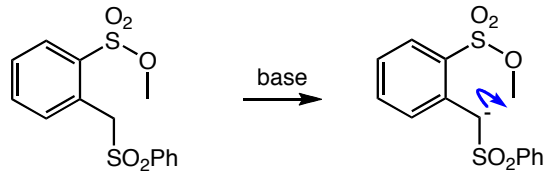
from **2**

4 Draw a possible mechanism of the conversion of the methyl sulfonate **1** into the sulfonate **2**.

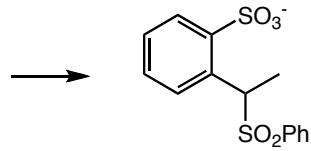


1 **2**

The simplest answer is an intramolecular process like this.



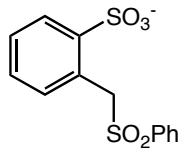
1



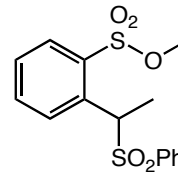
2

However, this is the *wrong* answer, and the following question hints at why this is so.

5 Significant amounts of the sulfonates **3** and the dimethyl derivative **4** form when the reaction shown in the previous question was stopped before completion. Show a revised mechanism that accounts for this.



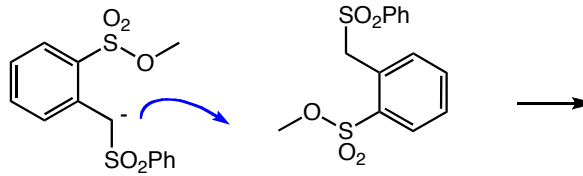
3



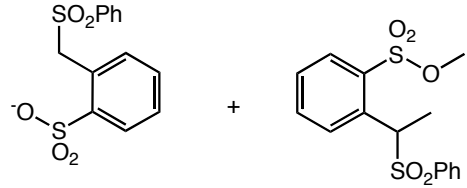
4

byproducts formed in significant amounts only when the reaction is stopped before completion

Formation of products **3** and **4** implies the mechanism is not intramolecular. In fact the sulfonate nucleophile cannot attain the ideal geometry to transfer methyl groups intramolecularly. This is a classic test of Baldwin's rules: 6-endo-tet closures are disfavored.



1 **1**



3 **4**