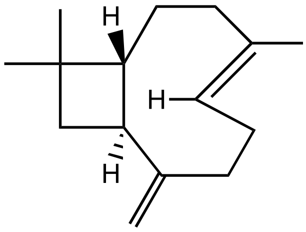
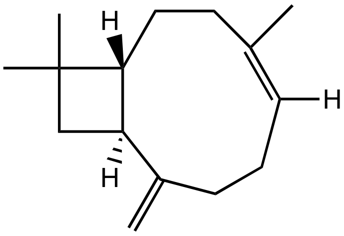
SECOND YEAR TUTORIAL PROBLEM

The geometrical isomers, caryophyllene, **1t**, and isocaryophyllene, **1c**, occur in many essential oils, especially clove oil.

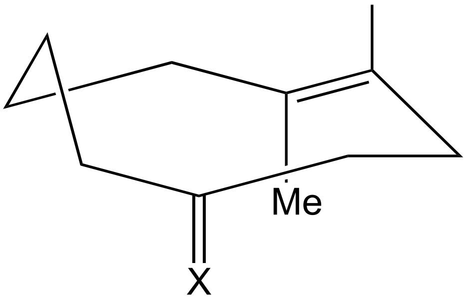


1t



1c

They may be easily separated by chromatography on silica gel impregnated with silver nitrate. Suggest a reason for this ease of separation .
What sort of reaction might allow the conversion of **1c** into **1t** ?
When they were isolated the absolute stereochemistries shown for **1t** and **1c** were not known. How many diastereoisomers (not enantiomers) were possible for **1t** before its absolute stereochemistry was determined ?
A couple of molecular modelling studies have suggested that one of the preferred conformations for the nine-membered ring in caryophyllene is that shown (**C**) below, with the methyl and methylene (X=CH_2) groups both pointing in the same direction:



C

The corresponding ketone, **C** (X = O), might be assumed to adopt a similar conformation. Give a reason why the following ^{1}H nmr data for the methyl and hydrogen on the internal double bond for caryophyllene and isocaryophyllene (which cannot take up this conformation) provide a little support for this assumption :

	δ, methyl	δ, hydrogen
caryophyllene ketone	1.76ppm	5.25ppm
isocaryophyllene ketone	1.62ppm	5.26ppm

Separate treatment with one reagent causes **1t** to react and leaves **1c** untouched, thus allowing an unambiguous identification of the two isomers. Which reagent is that and why does only **1t** react ? With reference to **C**(X = H_2) give the two possible products of the reaction of **1t** with that reagent .

The reaction of caryophyllene with **one equivalent** of HCl gives a product with **no** double bonds in it. With reference to **C**(X = CH_2) suggest a structure for this product .