

The corresponding ketone, **C** ($X = O$), might be assumed to adopt a similar conformation. Give a reason why the following 1H 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	1.76 ppm	5.25 ppm
isocaryophyllene ketone	1.62 ppm	5.26 ppm

*The methyl group resonance shows a slight downfield shift in **1t** compared to the corresponding value in **1c** which suggests that it may just be in the deshielding zone of the ketone group on the other side of the ring as appears to be the case from the conformation illustrated. The vinylic hydrogen shows no such shift, again as expected according to this conformation.*

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:

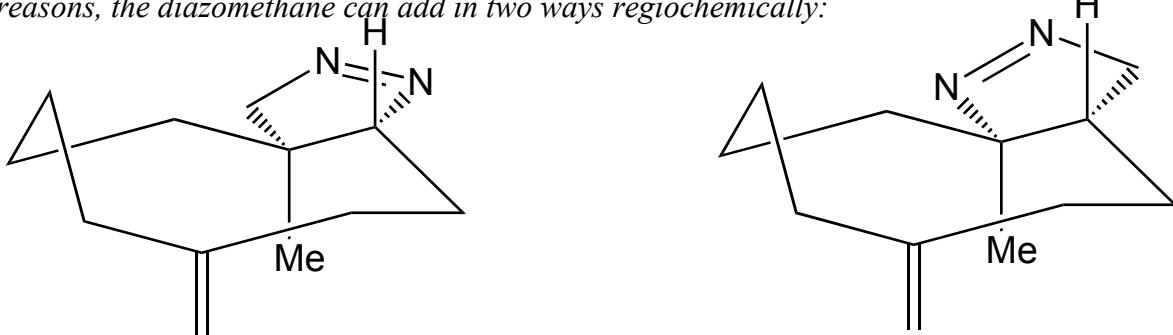


and why does only **1t** react?

*Diazomethane does not react with unactivated double bonds but the trans double bond in **1t** is sufficiently strained to be reactive enough.*

With reference to **C** ($X = H_2$) give the two possible products of the reaction of **1t** with that reagent:

Assuming that reaction occurs from outside of the ring, i.e. not across the ring for steric reasons, the diazomethane can add in two ways regiochemically:



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:

Assuming that the proton of the HCl attacks the most reactive trans double bond first to give the Markovnikov-derived cation, then this cation may, in turn, attack the methylene double bond to give a bicyclic cation, again in a Markovnikov manner, which is finally quenched with Cl^- :

