

Agenda:  
mechanism 101

- Arrow pushing
- Nucleophiles vs. Electrophiles
- Alkene: structures and Arrow pushing
- Regiochemistry

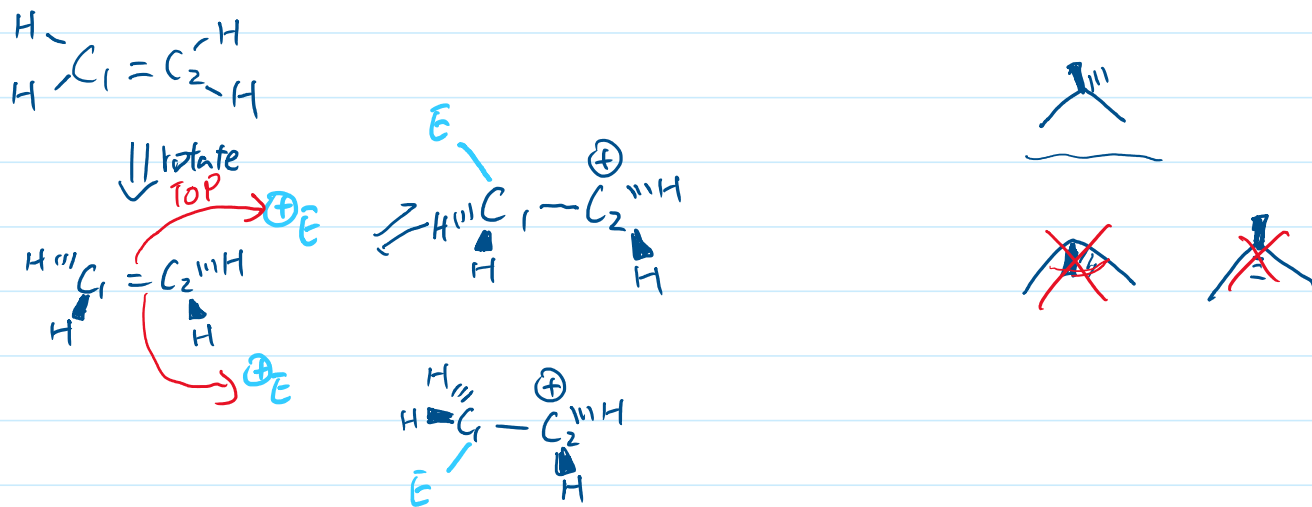
mechanism 102

- motive and opportunity
- Carbocations: stability, reactivity, and geometry
- Stereochemistry:

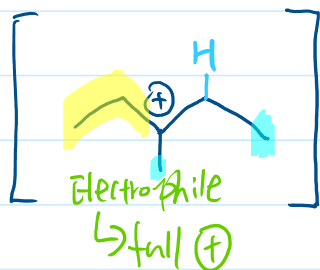
### REG11 Alkene Geometry: Flat

$E^{\oplus}$  = Generic electrophile (  $Br-Br$ ,  $H-Br$ ,  $CH_3^{\oplus}$  )

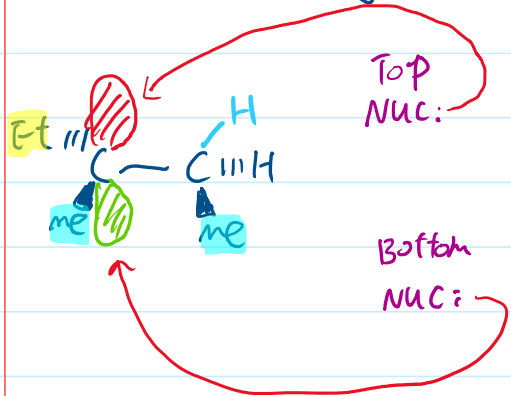
$E^{\oplus}$  Can add to the top or bottom face of alkenes



Since Carbocations are intermediates, they react further.



# Carbocation - Geometry: Flat



• nucleophiles can add to the empty  $2p^z$  orbital from Top or Bottom face w/ equal probability.

if: nucleophile =  $:\ddot{\text{Cl}}:^{\ominus}$ , then  $:\ddot{\text{Cl}}:^{\ominus}$  can add to the top or bottom faces

since  $\text{H}^{\oplus}$  (E<sup>+</sup>) and  $:\ddot{\text{Cl}}:^{\ominus}$  (Nuc) can add to the same face (both add to the top or bottom)

$\Downarrow$

SYN

or opposite faces  $\Rightarrow$  ANTI

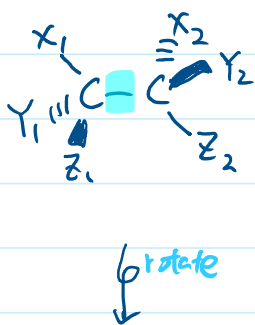
In the above e.g. (Alkene w/ HCl), the stereochemistry is MIXED

$\hookrightarrow$  Both syn and anti w/ equal probability.

stereochemistry: Cares the 3D space

tells us: how atoms will be "put on" and about chiral consequence

The direction of two groups relative to each other:



What groups are "anti" to one another?

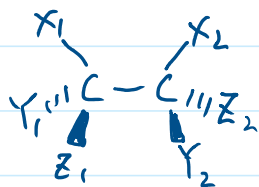
As drawn:

$X_1$  and  $Z_2$

$Y_1$  and  $Y_2$

$Z_1$  and  $X_2$

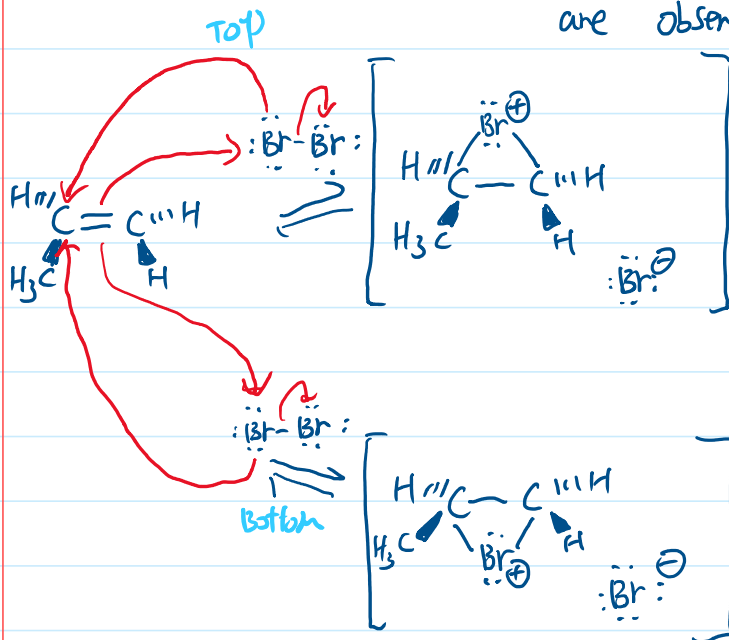
} are anti to each other



$X_1$  and  $X_2$   
 $Y_1$  and  $Z_2$   
 $Z_1$  and  $Y_2$

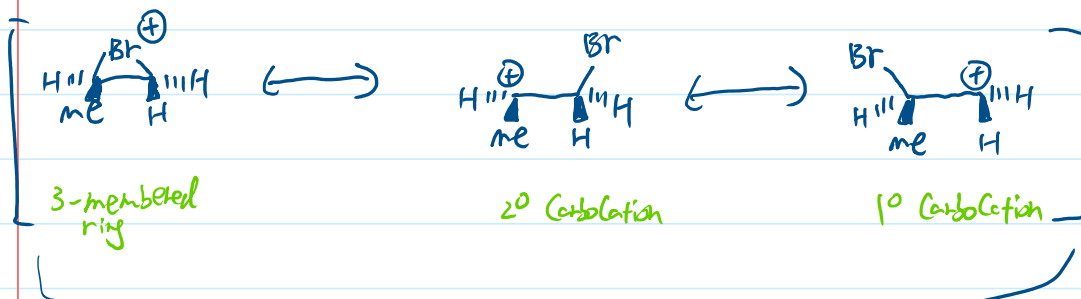
are syn

But in other reactions, only syn or only anti additions are observed. Why?

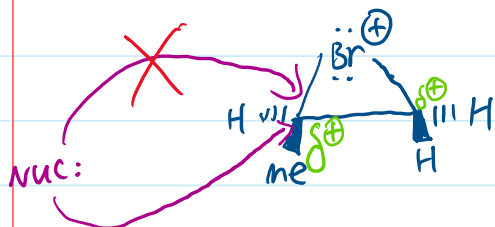


The bromonium ion intermediate has a bridging bromine (3-membered ring)

Why 3-membered ring? Delocalize charge  $\rightarrow$  stabilizing

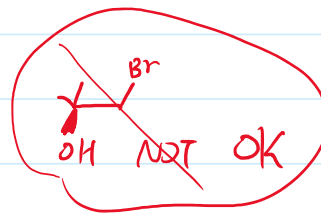
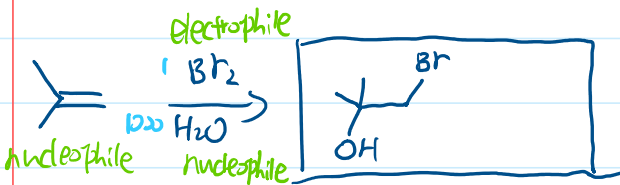
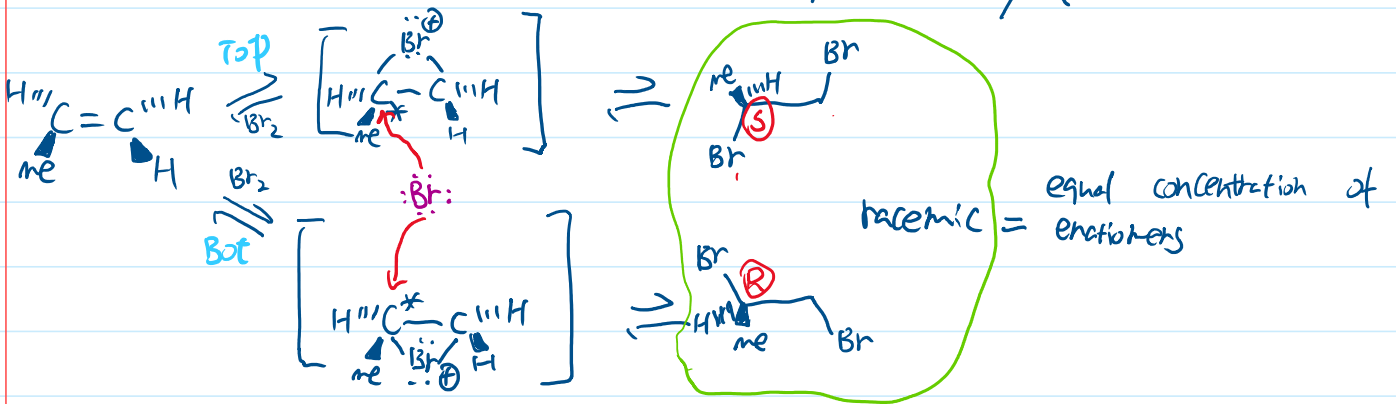
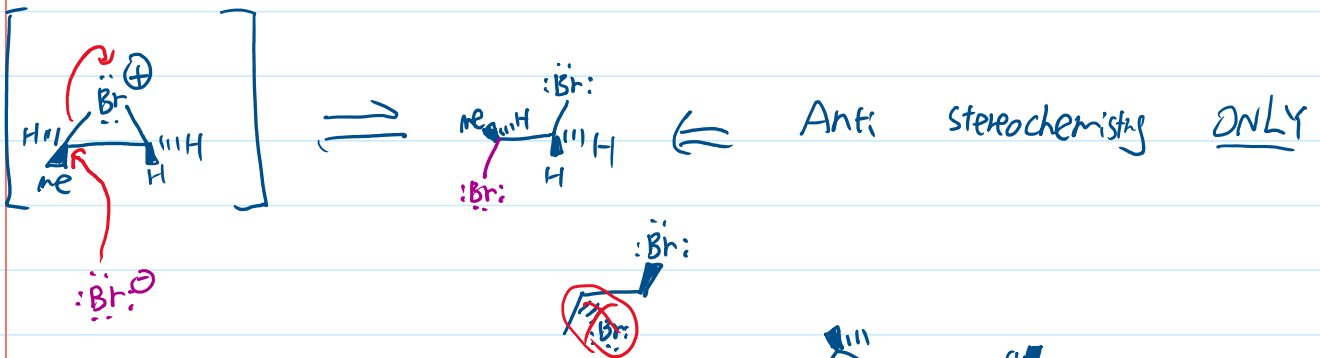


Bridging Br blocks NUC attack on the top face



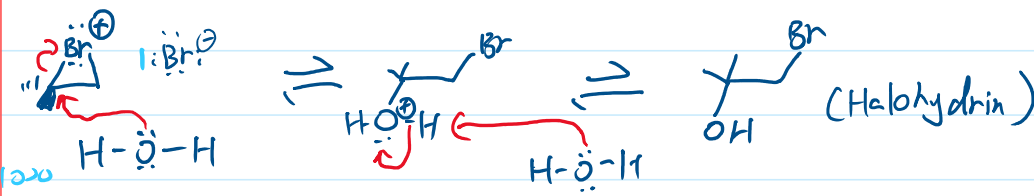
nucleophile will add to the more substituted C-atom,  
 b/c it has greater partial  $\oplus$

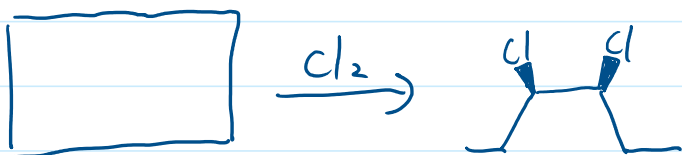
Now, the Nuc can only add to the more substituted C-atom from the backside of the bridging halide (Br-atom) b/c Br blocks top face.



Stereochemistry: Anti

$\Downarrow$

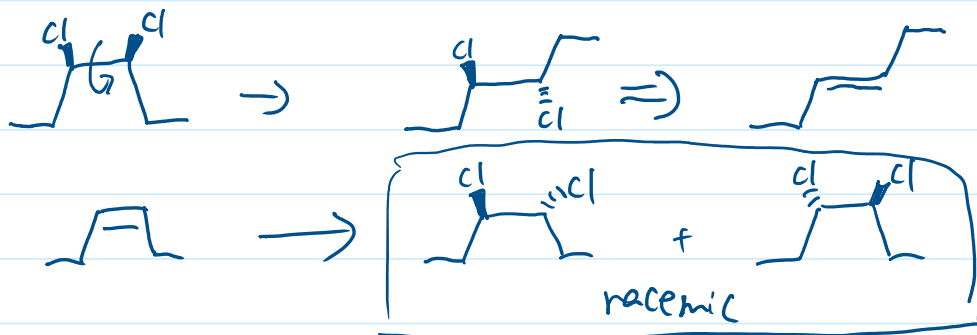




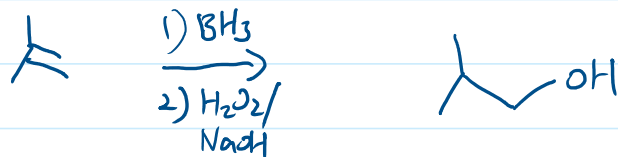
→ As drawn, Cl atoms are syn

→  $X_2$  + alkene stereochemistry of addition: Anti

Wut? Recall: single bonds can rotate!

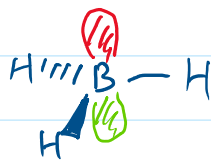


What about syn only additions?



Note: "1)" and "2)" matter! without them, it is wrong...

Consider  $BH_3$ :

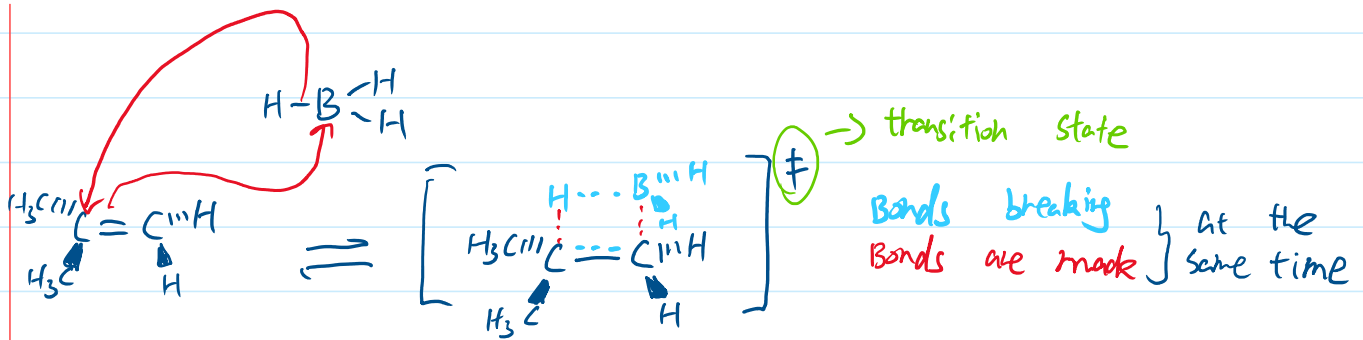


B has 6 valence  $e^-$ s

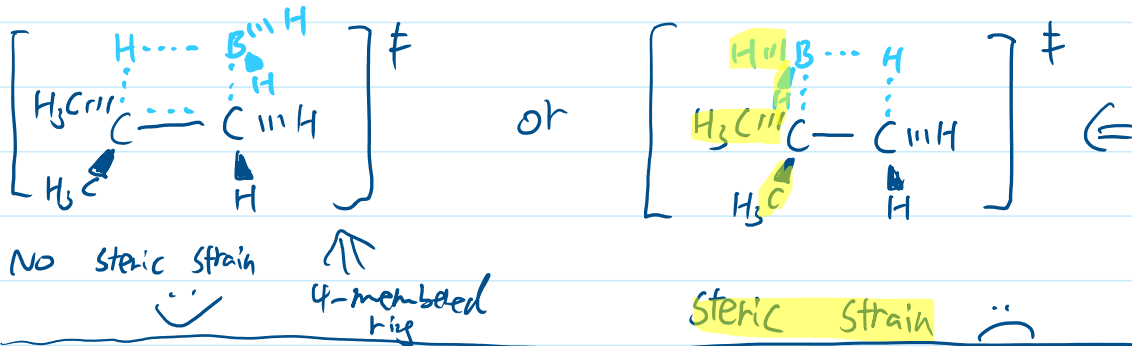
↓

empty 2p orbital

↳ electrophile



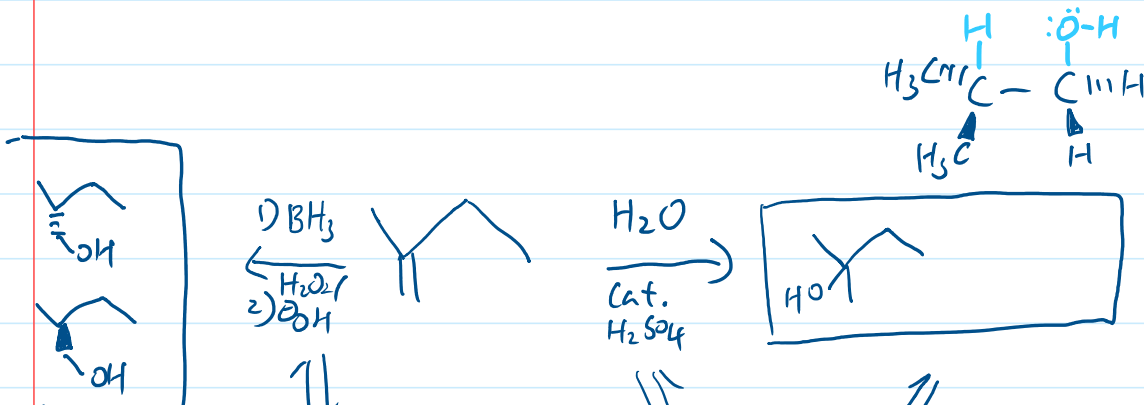
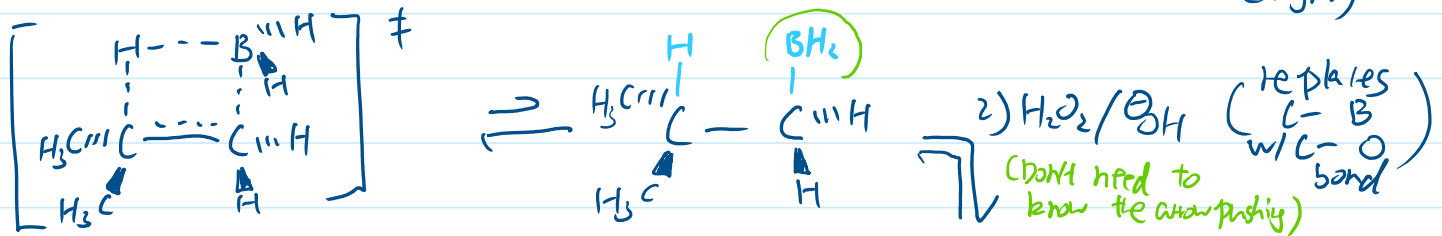
Why does B go to the less substituted C-atoms?

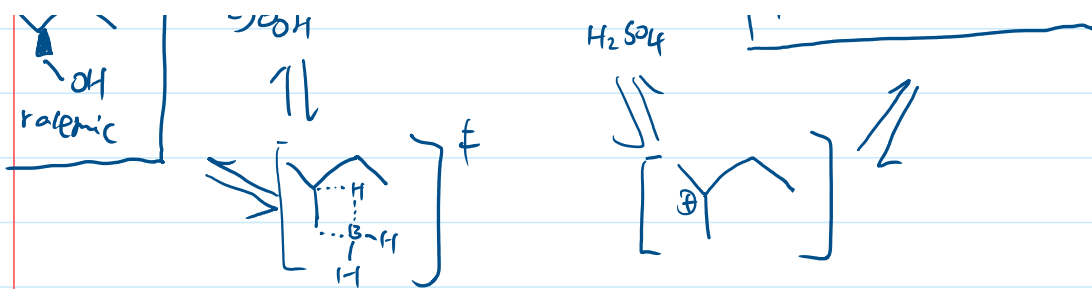


H- goes to more substituted C-atom  
 B- goes to the less substituted C-atom to avoid steric strain

### Non-Markovnikov regiochemistry

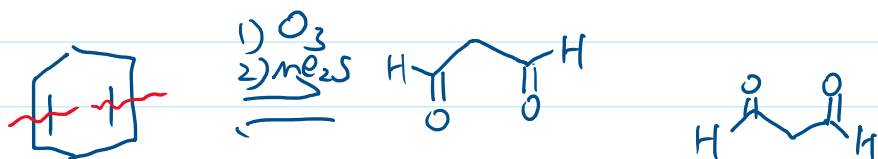
- The 4-membered ring transition state: the B and H can only add to the same face (syn)



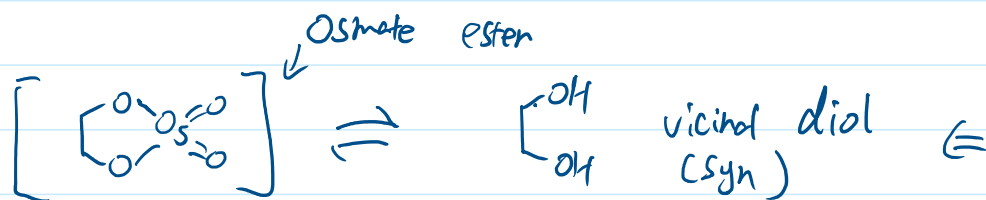


e.g.  $\text{O}_3$ ,  $\text{OsO}_4 \Rightarrow$  Do not need to know arrow pushing.

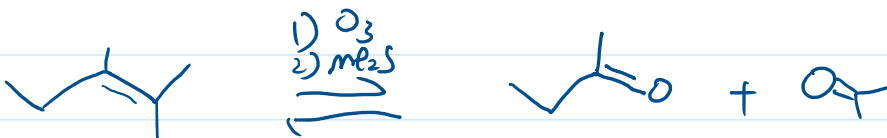
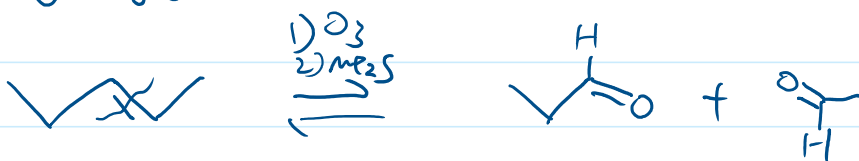
$\text{O}_3$  (ozonolysis) = scissor



$\text{OsO}_4$ :



e.g. ozonolysis



ozonolysis: 1)  $\text{O}_3$  2)  $(\text{CH}_3)_2\text{S} \equiv \text{Me}_2\text{S}$