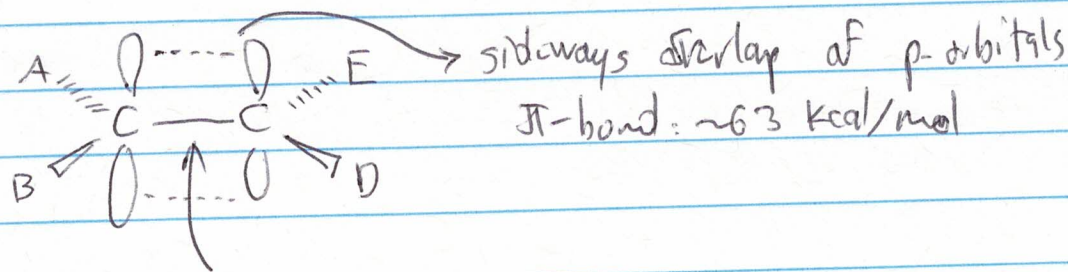


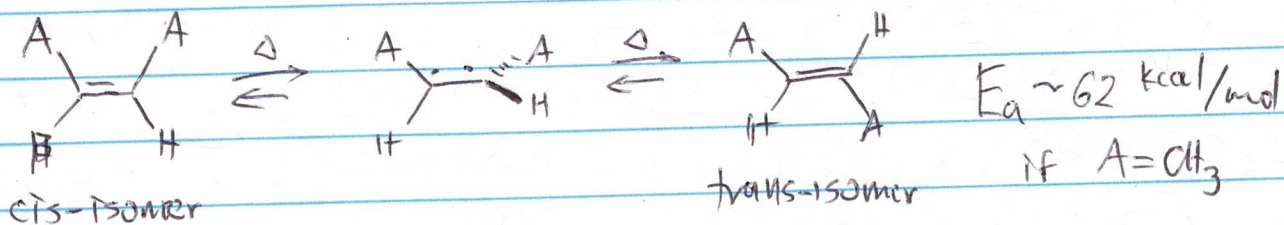
Lecture XV: Diastereomers of Alkenes

02-19-2020

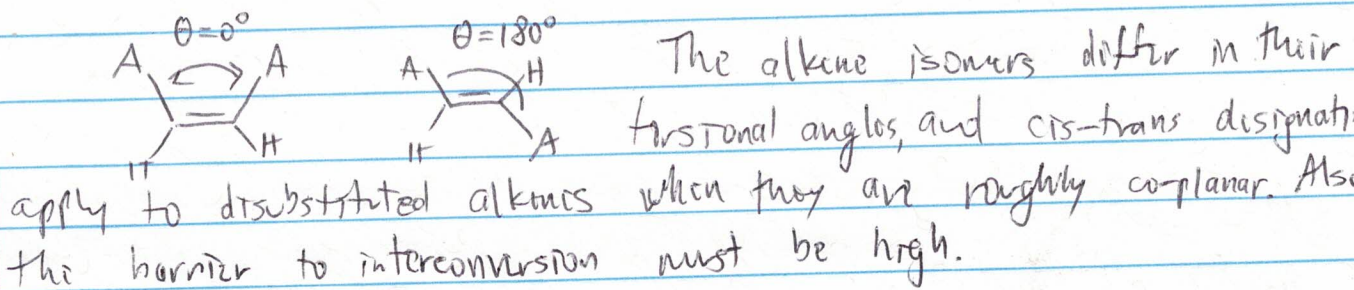
Alkenes are a broad class of generally planar compounds, which can show cis-trans isomerism:



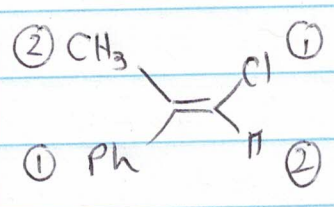
σ -bond between sp^2 hybridized carbons
 ~ 83 kcal/mol



Cis/trans isomers are stable, configurational isomers. They are diastereomers of one another:

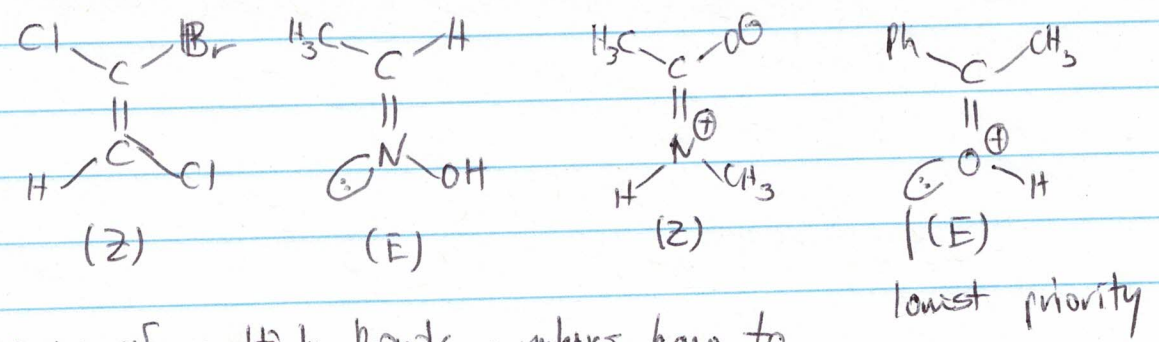


E/Z nomenclature is more general and it applies to a greater range of substitution patterns.

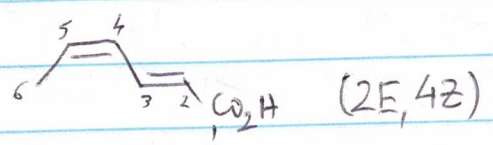


According to CIP rules. If ①s are on the same side \Rightarrow Z (zusammen, together)
 ①s on opposite sides \Rightarrow E (entgegen, opposite)

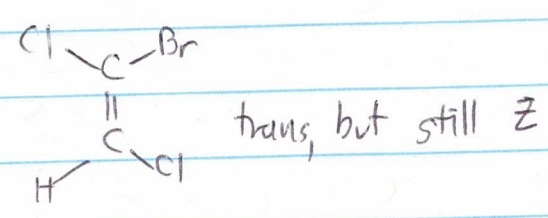
This nomenclature applies to other double bonds too:



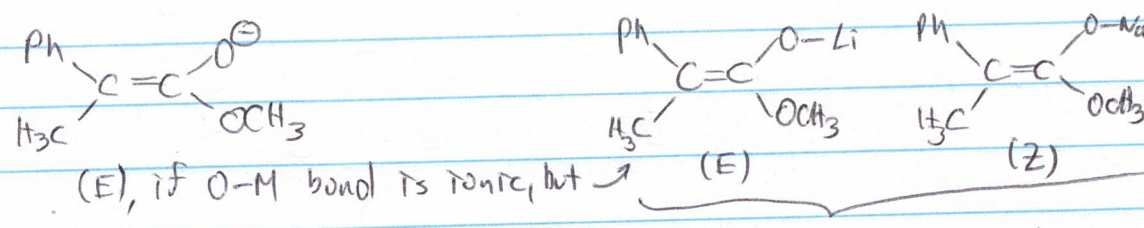
In cases of multiple bonds, numbers have to be assigned too:



Z and E do not always correspond to cis and trans:

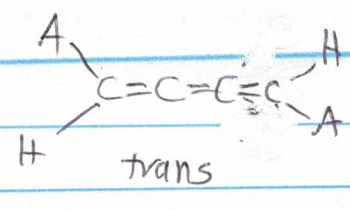
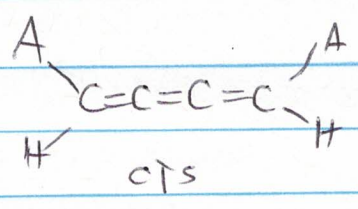


In the case of enolates, things can get confusing:

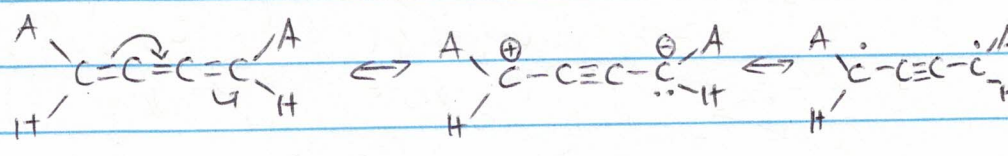


not recommended; instead, stick with the local cis/trans relationships

Cumulenes also have stereoisomers



They are more easily equilibrated

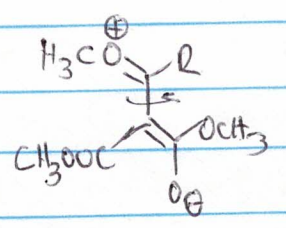
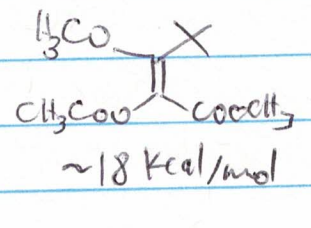
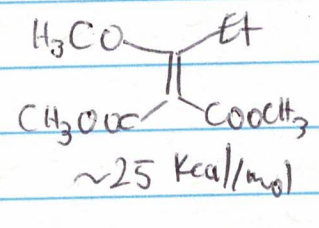
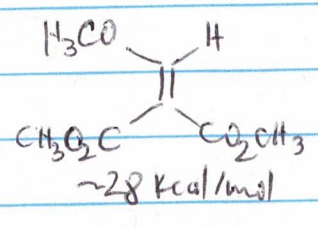
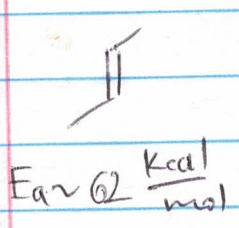


[3]cumulene barriers are 27-31 kcal/mol

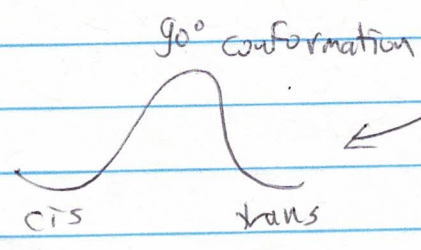
[5] " " " even lower, ~19 kcal/mol

[7] and [9]cumulenes polymerize quickly and their barriers are unknown

Some alkenes will also have low rotational barriers, and some are not going to be planar either. The two are often related:

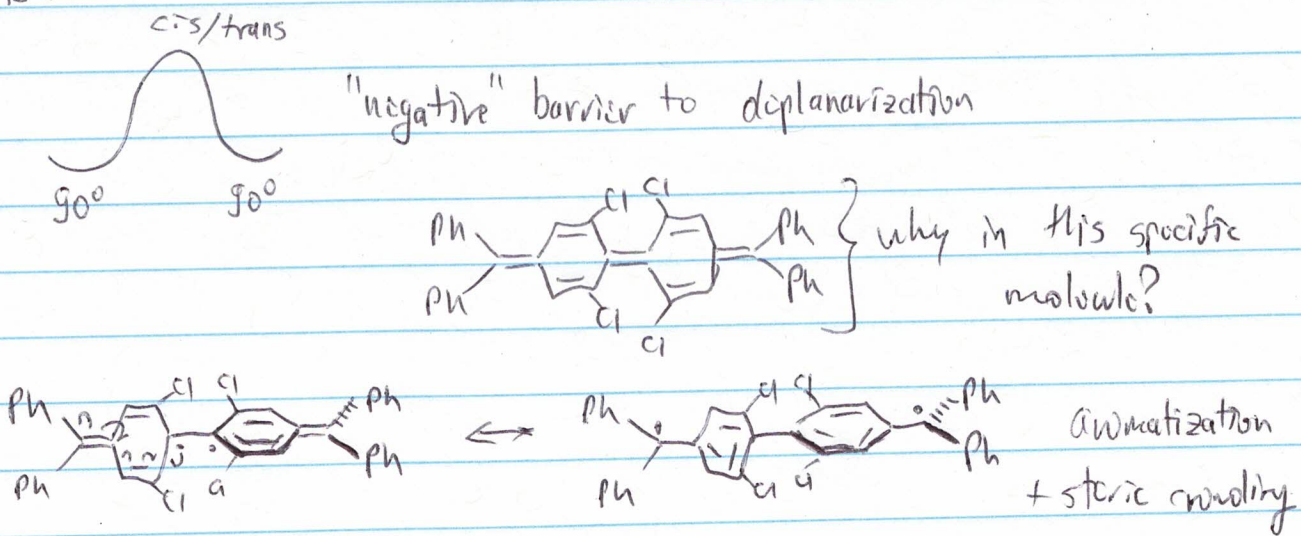


Free rotation is a consequence of both steric crowding and a favorable resonance structure



This is the common situation

But in severely crowded alkenes, coplanarity becomes a transition state:

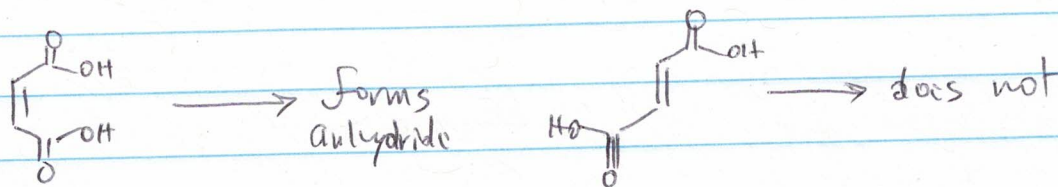


X X X X is a hypothetical molecule, so far not prepared predicted to be twisted by 45°, with a ~~rotation~~ singlet barrier triplet split of ~15 kcal/mol

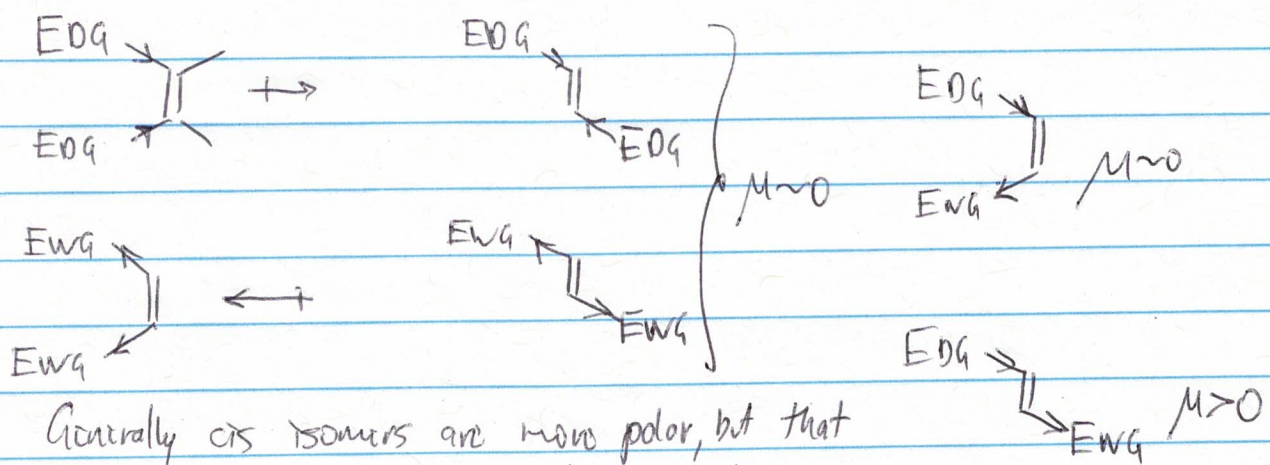
Struct. Chem. 2006, 17, 419

Methods to Distinguish Cis/trans Isomers

Chemical methods used to be very commonly employed, but are now largely outdated.



Physical methods are much more common and useful today
Dipole moments differ:

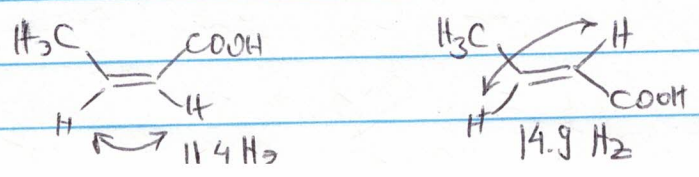


Generally cis isomers are more polar, but that will depend based on whether the attached groups are similar or different in their electron-donating character.

This difference in dipole moments affects the IR and Raman spectra too. In IR, symmetrically substituted trans-alkenes are not visible, since μ remains zero; cis-substituted ones are. In the case of broken symmetry, cis-isomers still have higher intensity bands.

NMR can tell a bit ~~by~~ ~~conf~~ about configuration by looking at chemical shifts, but in the case of non-equivalent protons, 3J coupling constants are a lot more diagnostic.

$\begin{matrix} \text{X} & & \text{Y} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{R}_1 & & \text{R}_2 \end{matrix}$	$\begin{matrix} \text{X} & & \text{R}_2 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{R}_1 & & \text{Y} \end{matrix}$
$\text{X}=\text{Y}=\text{H}, \quad ^3J = +4 \text{ to } +12 \text{ Hz}$	$^3J = +12 \text{ to } +19 \text{ Hz}$
$\text{X}=\text{Y}=\text{F}, \quad ^3J = +15 \text{ to } +35 \text{ Hz}$	$^3J = -115 \text{ to } -135 \text{ Hz}$
$\left. \begin{matrix} \text{X}=\text{H} \\ \text{Y}=\text{F} \end{matrix} \right\} \quad ^3J = -4 \text{ to } +20 \text{ Hz}$	$^3J = +10 \text{ to } +50 \text{ Hz}$



In the cases where you don't have coupling nuclei, the following formula for chemical shifts can be used:

$$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{trans} + Z_{cis}$$

↑ ↑
these generally differ for most substituents

TABLE 9.5. Parameters for Calculation of Proton Shift in the Alkene^a Shown in Figure 9.39

Substituent R	Z _i for R (ppm)		
	Z _{gem}	Z _{cis}	Z _{trans}
-H	0	0	0
-Alkyl	0.45	-0.22	-0.28
-Alkyl-Ring	0.69	-0.25	-0.28
-CH ₂ O	0.64	-0.01	-0.02
-CH ₂ S	0.71	-0.13	-0.22
-CH ₂ X; X = F, Cl, Br	0.70	0.11	-0.04
-CH ₂ N	0.58	-0.10	-0.08
-C=C isolated	1.00	-0.09	-0.23
-C=C conjugated	1.24	0.02	-0.05
-C≡N	0.27	0.75	0.55
-C≡C	0.47	0.38	0.12
-C=O isolated	1.10	1.12	0.87
-C=O conjugated	1.06	0.91	0.74
-CO ₂ H isolated	0.97	1.41	0.71
-CO ₂ H conjugated	0.80	0.98	0.32
-CO ₂ R isolated	0.80	1.18	0.55
-CO ₂ R conjugated	0.78	1.01	0.46
H			
-C=O	1.02	0.95	1.17
N			
-C=O	1.37	0.98	0.46
Cl			
-C=O	1.11	1.46	1.01
-OR, R: aliphatic	1.22	-1.07	-1.21
-OR, R: conjugated	1.21	-0.60	-1.00
-OCOR	2.11	-0.35	-0.64
-CH ₂ -C=O; -CH ₂ -C≡N	0.69	-0.08	-0.06
-CH ₂ -Aromatic ring	1.05	-0.29	-0.32
-Cl	1.08	0.18	0.13
-Br	1.07	0.45	0.55
-I	1.14	0.81	0.88
-N-R, R: aliphatic	0.80	-1.26	-1.21
-N-R, R: conjugated	1.17	-0.53	-0.99
-N-C=O	2.08	-0.57	-0.72
-Aromatic	1.38	0.36	-0.07
-Aromatic o-subst	1.65	0.19	0.09
-SR	1.11	-0.29	-0.13
-SO ₂	1.55	1.16	0.93

^a From Matter, Simon, Sternhell, et al. (1969). Adapted, with permission, from Matter, E.V. et al., *Tetrahedron* (1969), 25, 693/4. Copyright © 1969 Pergamon Press, Headington Hill, Oxford, UK.