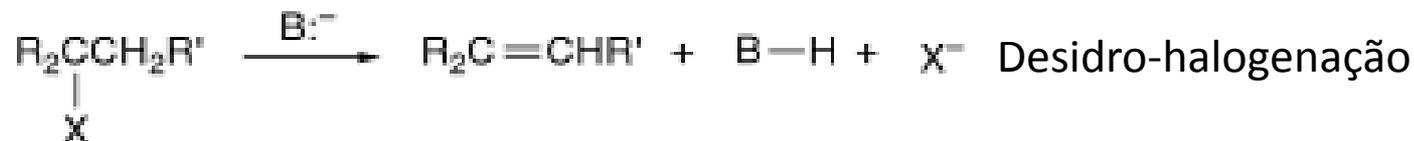
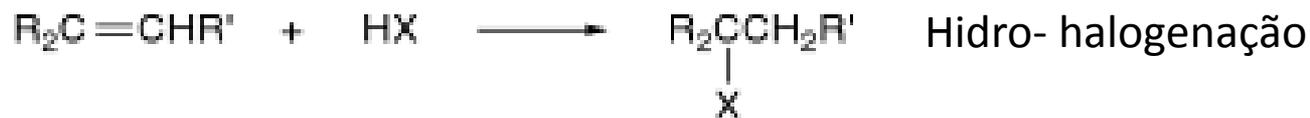
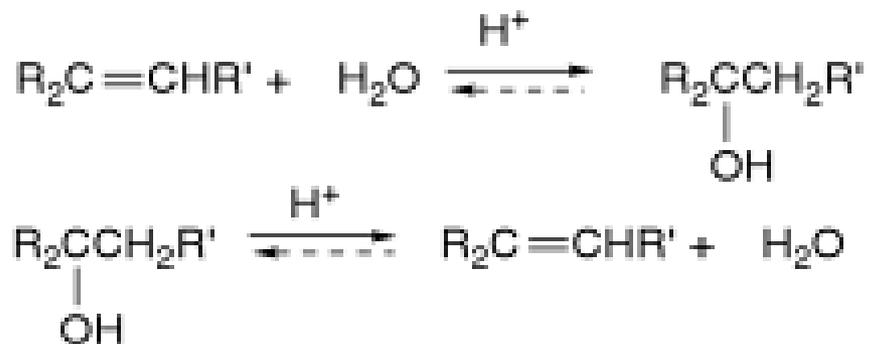


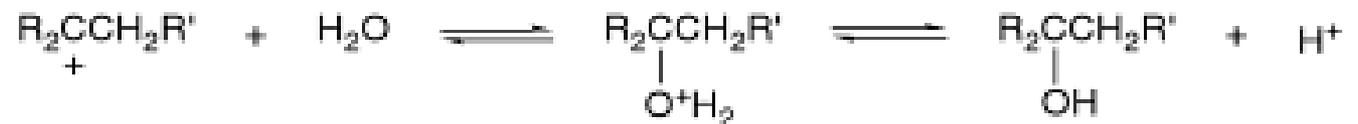
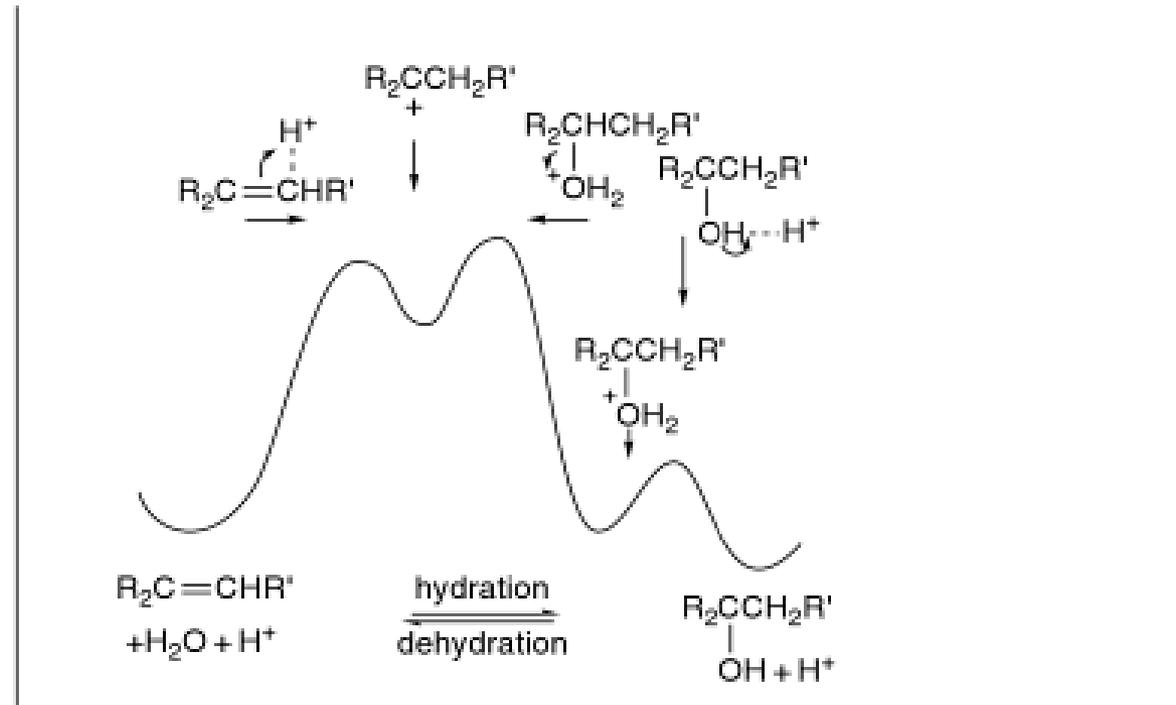
**Adição polar e reações
de eliminação
(Outras adições
concertadas e radicalares
serão vistas mais tarde)**

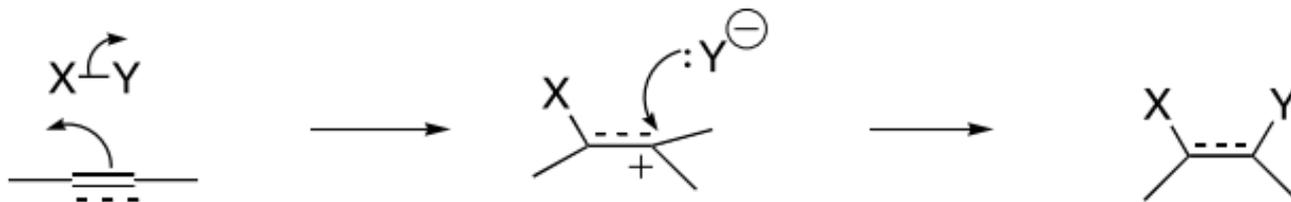
Reações de adição e eliminação são processos inversos e há uma relação entre elas.



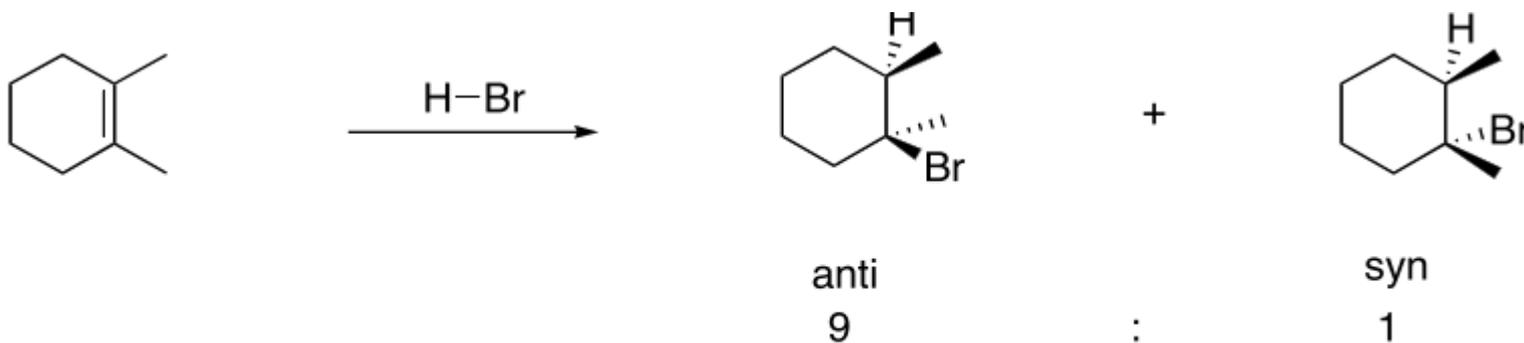
Princípio da reversibilidade microscópica e neste casos ambos seguem mesmo caminho mecanístico mas em direções opostas assim as conclusões da adição serve para eliminação

Adição eletrofílica bimolecular

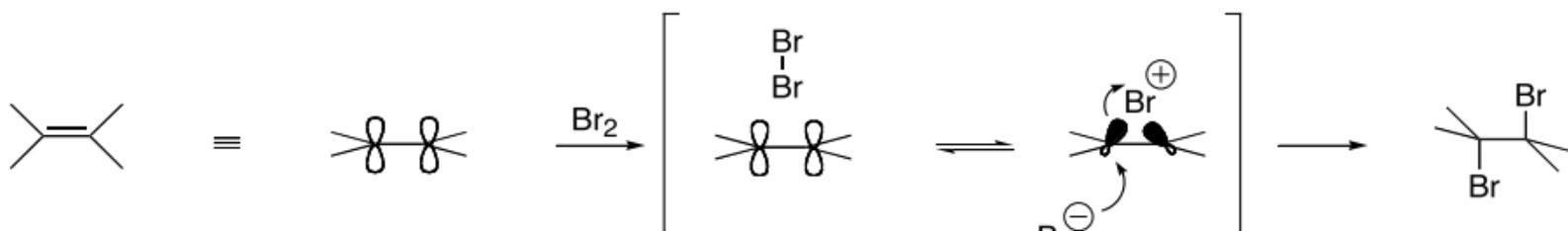
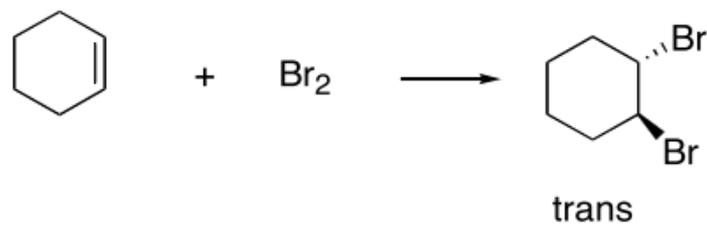




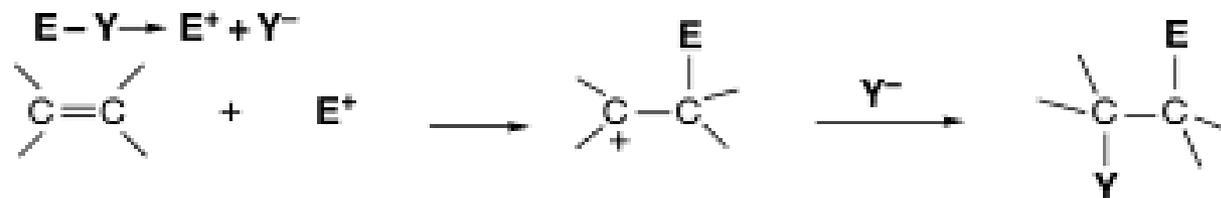
Questões
 Estereoquímica
 Regioquímica
 mecanismo



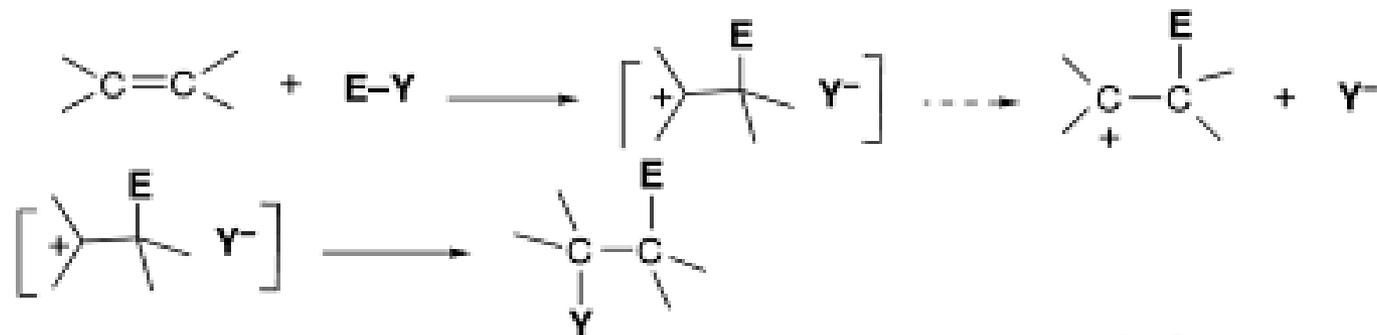
Hammond, *JACS* **1954**, 76, 4121



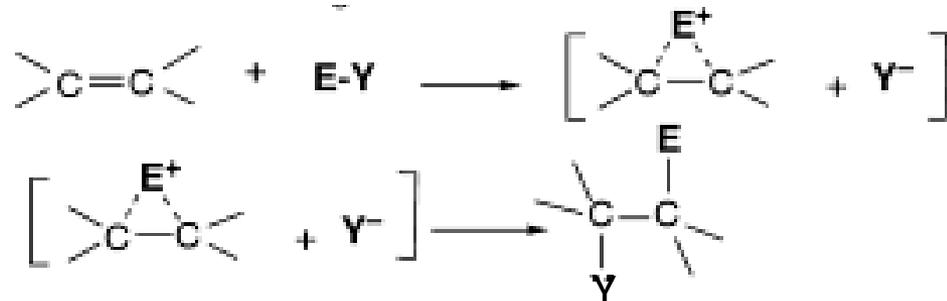
A.



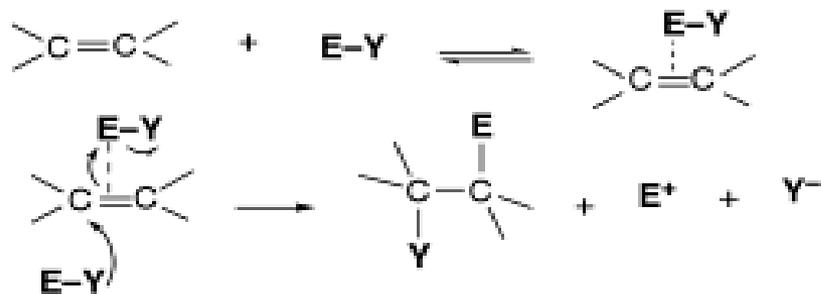
B.



C.



D



Mecanismos possíveis para adição eletrofílica

Adição de HX a alcenos



Regiosseletiva porém esta regioquímica pode ser complicada quando ocorrer adição radicalar junto com adição iônica.

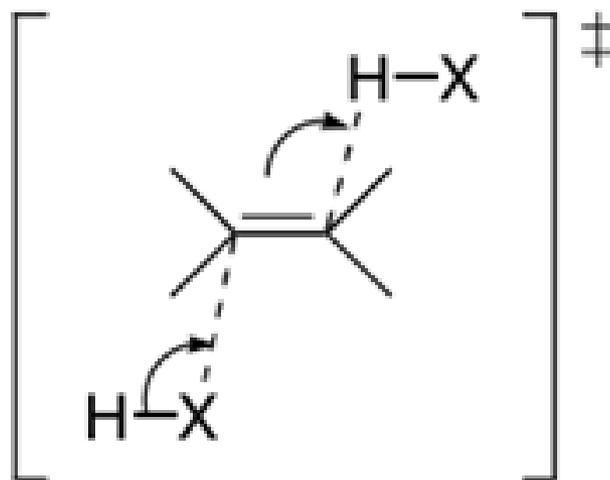
Quando for regioespecífica dará somente uma regioquímica

Reatividade $\text{HI} > \text{HBr} > \text{HCl}$ e a equação de velocidade é de ordem 3.

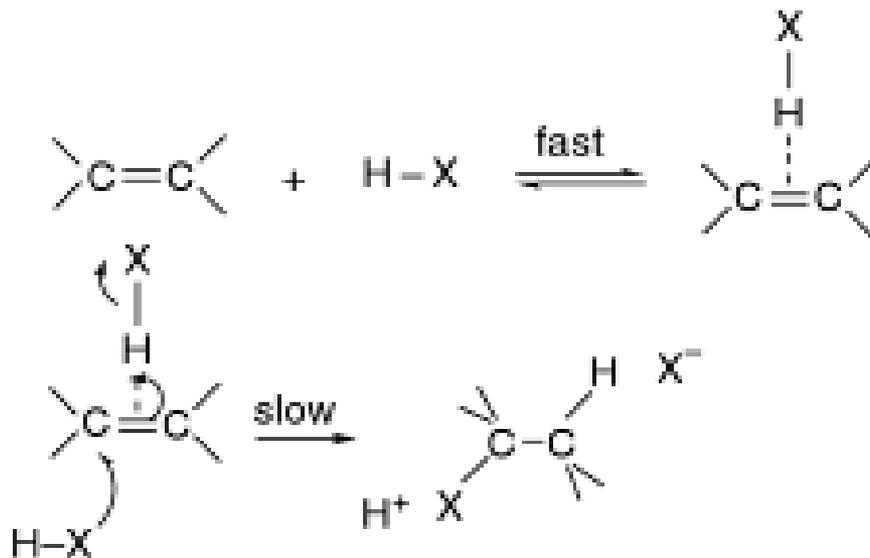
Como explicar

cinética normalmente é de terceira ordem Ad_E3

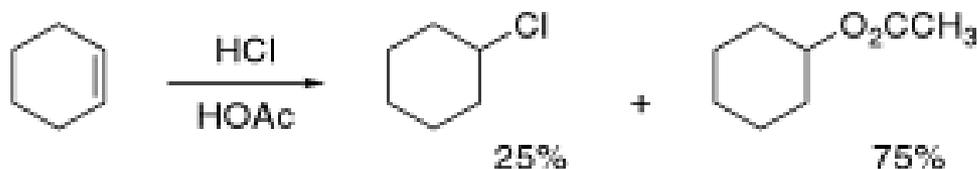
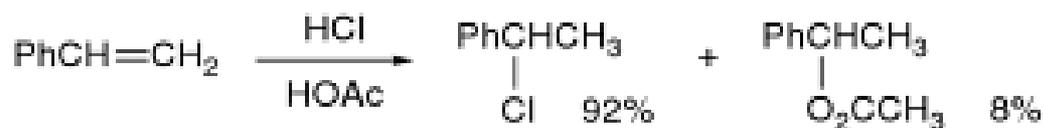
$$v = k_3[\text{alceno}][\text{H-X}]^2$$



possibilidade

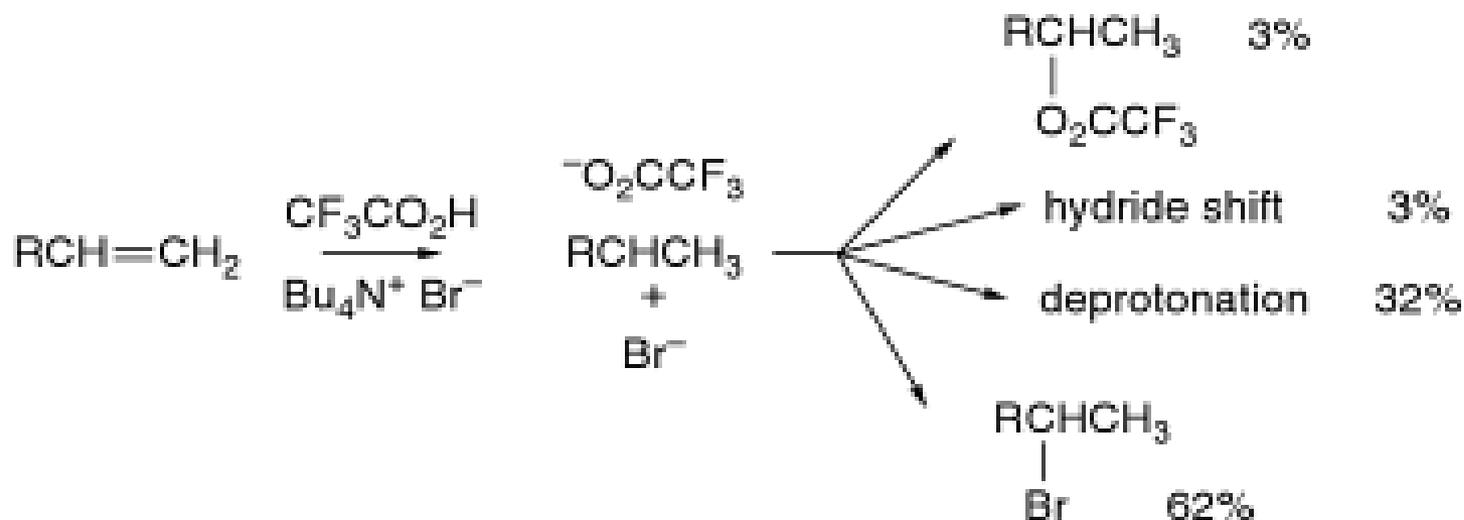


Quando o alceno é conjugado o mecanismo pode mudar como no caso do estireno que apresenta um cinética de primeira ordem para o HCl indicando que somente o HCl participa da etapa lenta da reação portanto o caso A

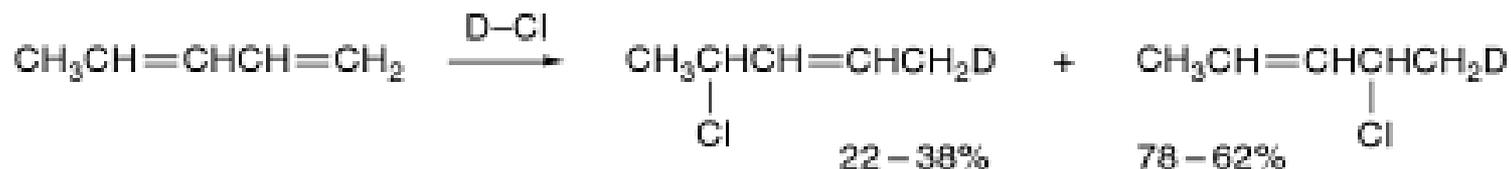


Reações que competem quando tem solventes nucleofílicos e existem rearranjos devido a formação carbocátions

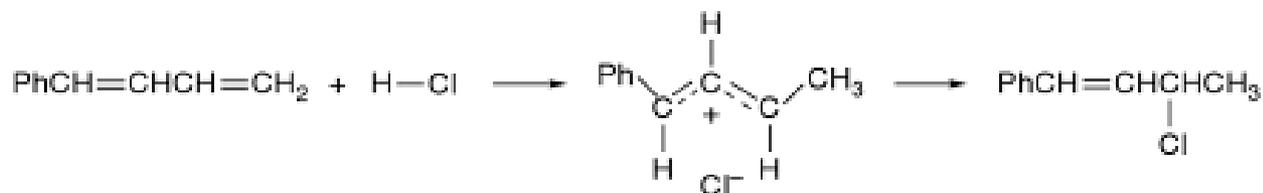
Formação de de um sandwiche de íons nos intermediarios chave das reações de HBr em ácido trifluoroacético com 1, 2 , ou 4- octeno.



Com dienos a adição pode ser 1,2 ou 1,4 e o mecanismo de par iônico é favorecido pela estabilização do íon alílico

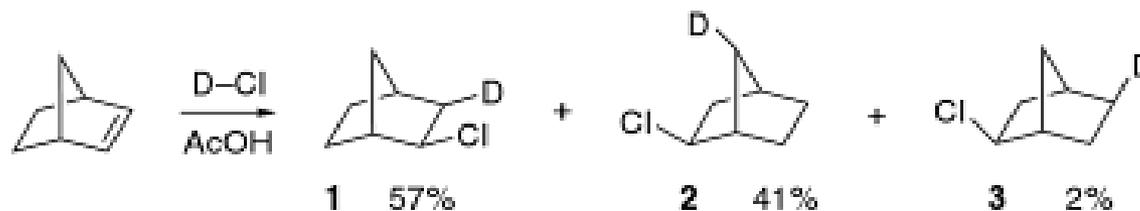
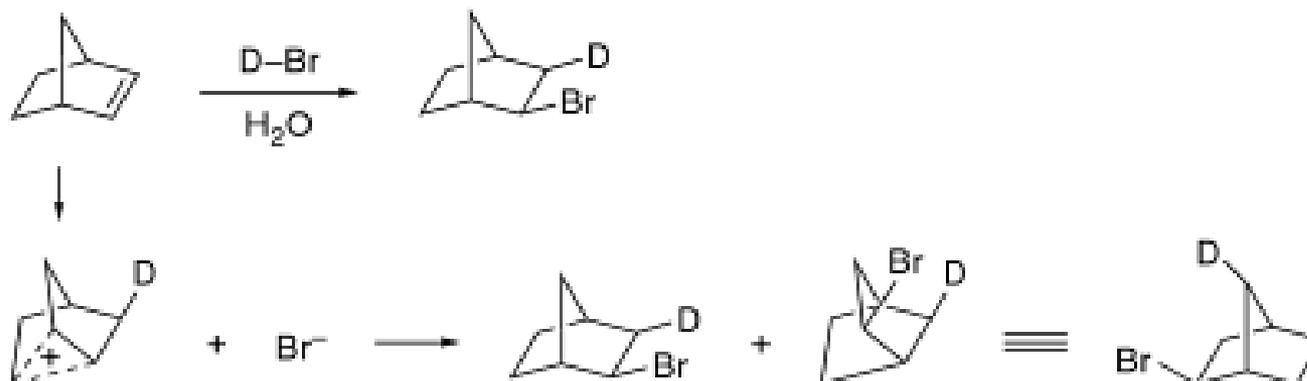


Com 1-fenil -3,4-butadieno somente um produto de adição em 3,4



Cinética Ad_E2

No caso de adição HCl ou HBr a norborneno



The Addition of Hydrogen Chloride and Hydrobromic Acid to 2,3-Dideuterionorbornene

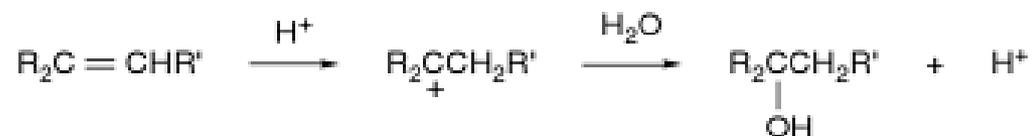
J. K. Stille,^{1a} Fred M. Sonnenberg,^{1b,c} and Thomas H. Kinstle

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52240, and the Department of Chemistry, Iowa State University, Ames, Iowa. Received June 17, 1966

Abstract: The synthesis of 2,3-dideuterionorbornene and the ionic addition of hydrogen halides to it have been carried out. From the reaction of hydrogen chloride, about 50% of the product results from *exo-cis* addition without rearrangement. Of the portion of the product formed as a consequence of rearrangement, 38% arises from a 6,2-hydride shift and 12% from a Wagner–Merrwein rearrangement. In the reaction with hydrobromic acid, the percentages are 40, 46, and 14, respectively. Dehydrohalogenation of the *exo*- and *endo*-2-halonorbornanes occurs nearly exclusively by abstraction of the *exo*-vicinal proton by base. The mechanistic interpretation of these results is discussed.

O fato de 1 ser diferente de 2 indica que o intermediario não simétrico e que par iônico forma adição sin antes do ion não clássico atingir a simetria

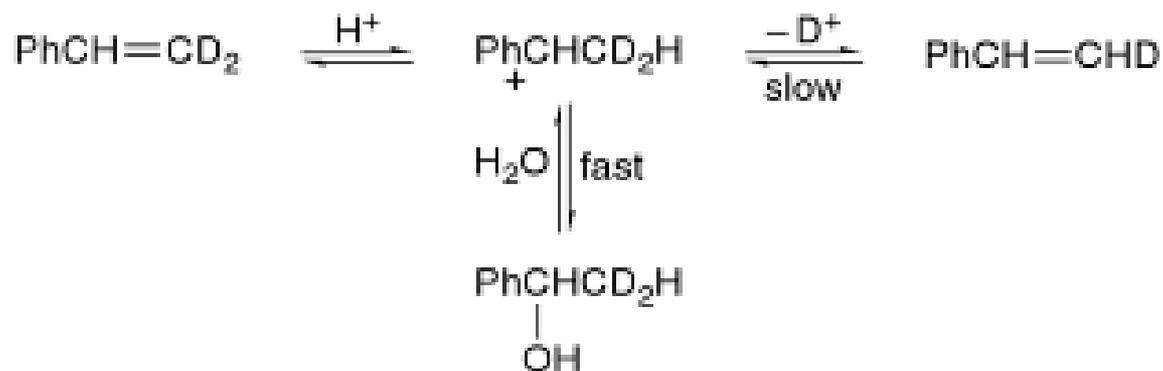
HIDRATAÇÃO E REAÇÕES ANÁLOGAS

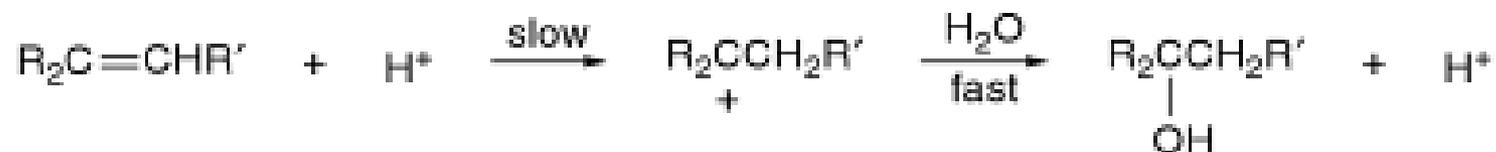


Segue a regra de Markovnikoff

Porém para responder se há realmente um cation ou será que o nucleófilo fica envolvido antes da completa transferencia do proton

$$k_{H_2O}/k_{D_2O} = 2-4$$





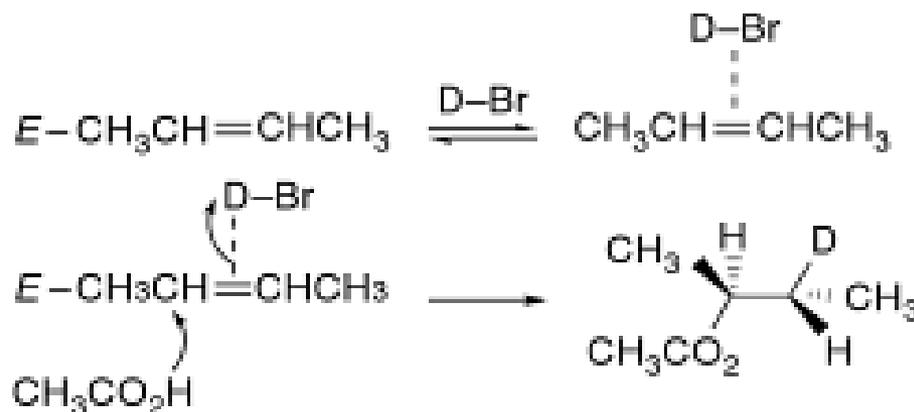
Alcenos sem substituintes fenilas seguem mecanismo análogo

Velocidades de hidratação de alcenos em ácidos sulfúrico aquoso

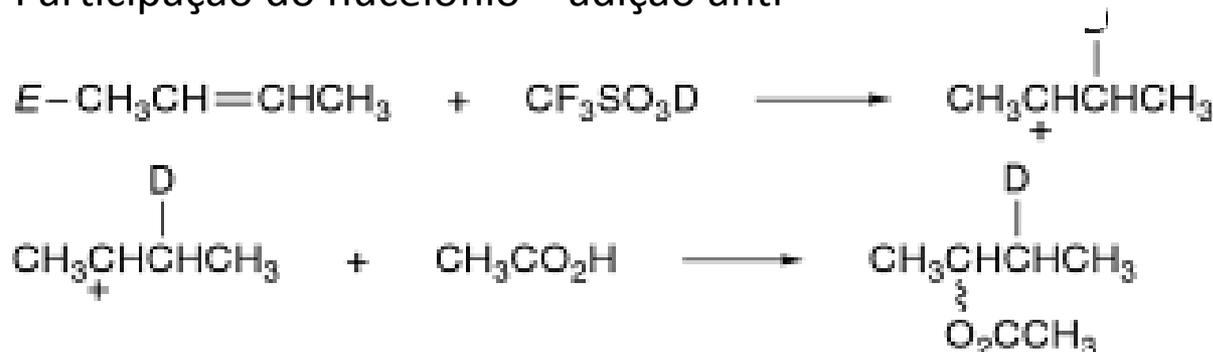
Alcenos	$k_2 (M^{-1} s^{-1})$	k_{rel}
$CH_2=CH_2$	1.56×10^{-15}	1
$CH_3CH=CH_2$	2.38×10^{-8}	1.6×10^7
$CH_3(CH_2)_3CH=CH_2$	4.32×10^{-8}	3.0×10^7
$(CH_3)_2C=CHCH_3$	2.14×10^{-3}	1.5×10^{12}
$(CH_3)_2C=CH_2$	3.71×10^{-3}	2.5×10^{12}
$PhCH=CH_2$	2.4×10^{-6}	1.6×10^9

a. W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 7233 (1977).

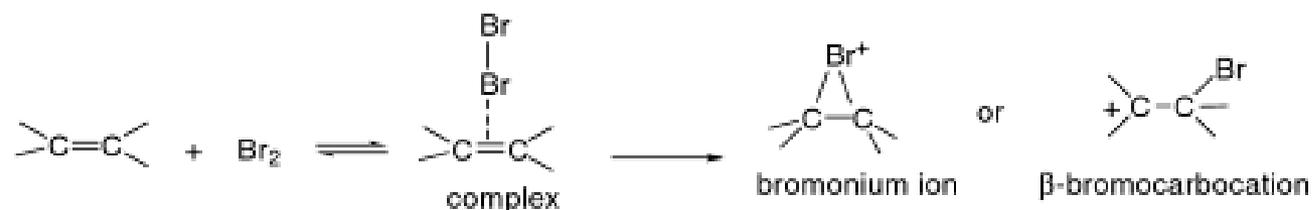
Com outros solvente nucleofílicos com catálise de catálise de ácidos fortes é semelhante a hidratação com o solvente substituindo a água como nucleófilo



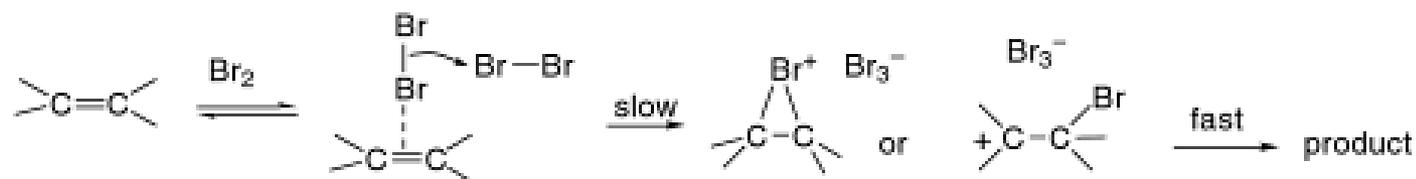
Participação do nucleófilo – adição anti



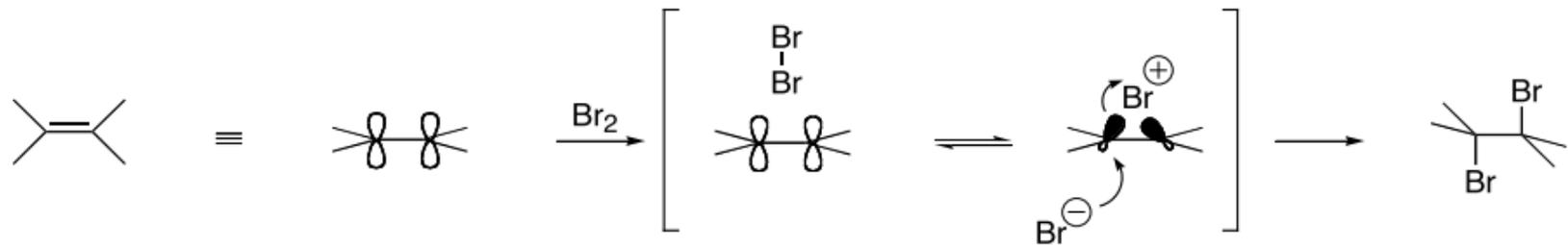
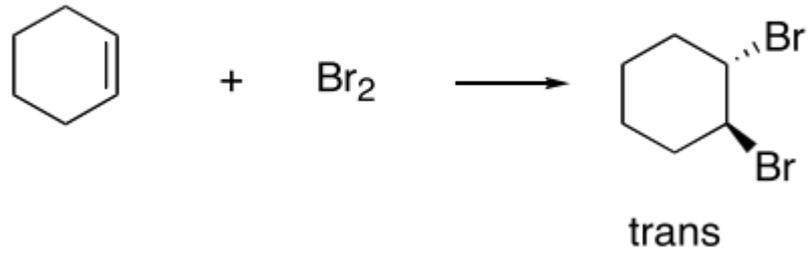
Sem participação do nucleófilo a adição não é estereoespecífica e com ácido trifluoroacético que não precisa de outro ácido forte e a reação ocorre com forte efeito isotópico com ácido deuterado



$$\text{Rate} = k_1[\text{alkene}][\text{Br}_2] + k_2[\text{alkene}][\text{Br}_2]^2 + k_3[\text{alkene}][\text{Br}_2][\text{Br}^-]$$



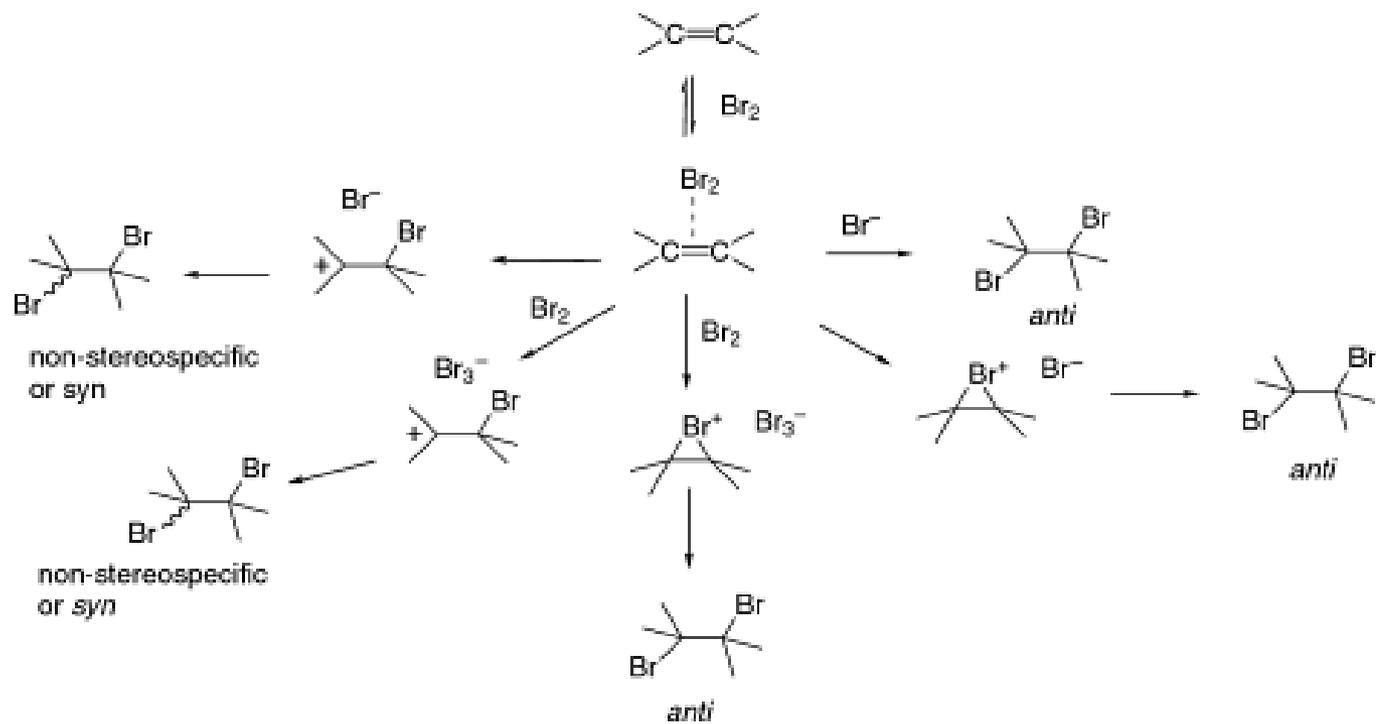
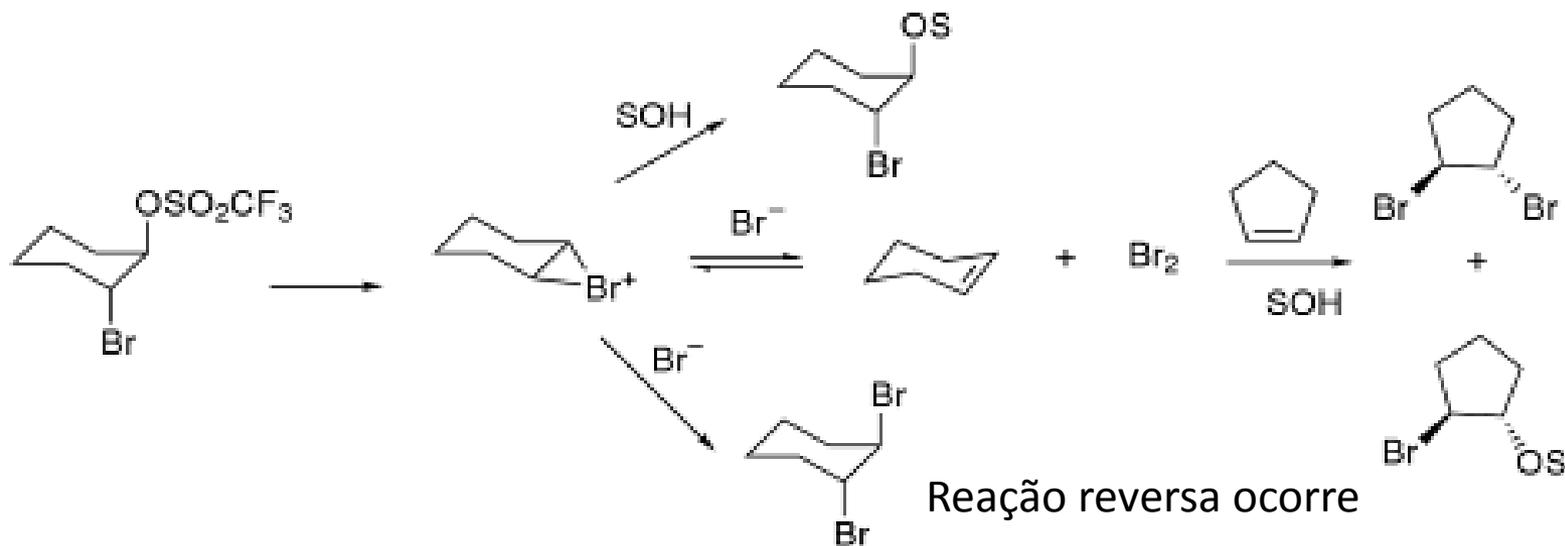
Adição de halogênios



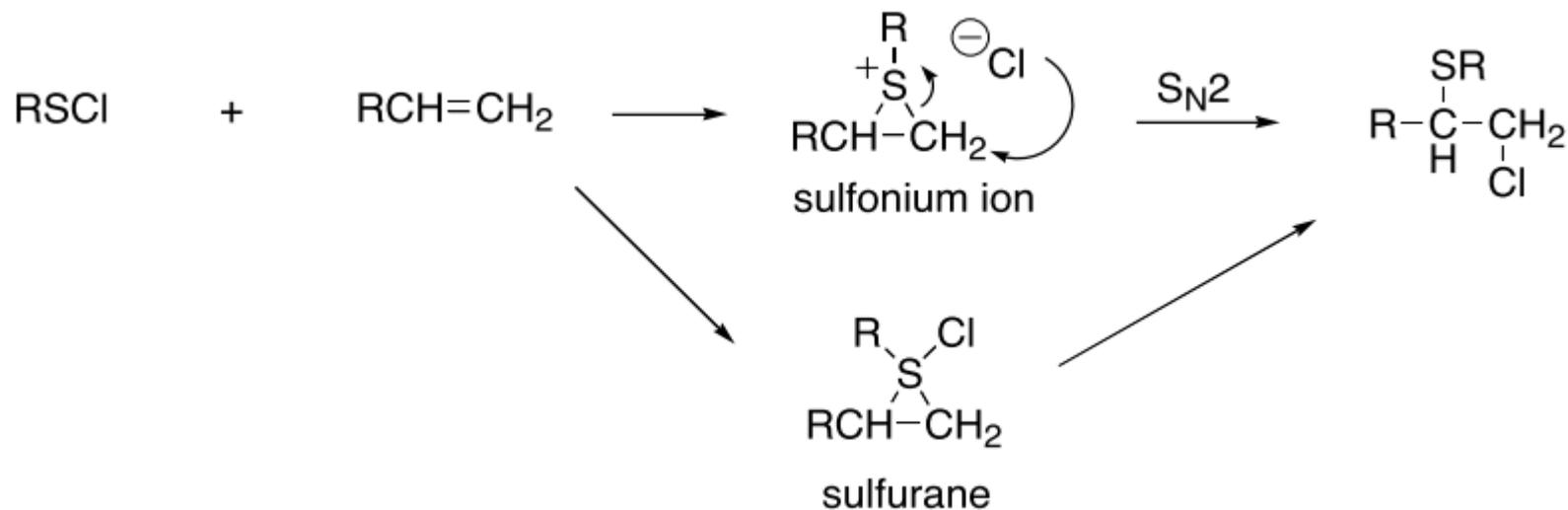
Reatividade relativa dos alcenos frente a halogenação

	Chlorination ^a	Bromination ^b	Bromination ^c
Ethene		0.01	0.0045
1-Butene	1.00	1.00	1.00
3,3-Dimethyl-1-butene	1.15	0.27	1.81
Z-2-Butene	63	27	173
E-2-Butene	50	17.5	159
2-Methylpropene	58	57	109
2-Methyl-2-butene	1.1×10^4	1.38×10^4	
2,3-Dimethyl-2-butene	4.3×10^5	19.0×10^4	

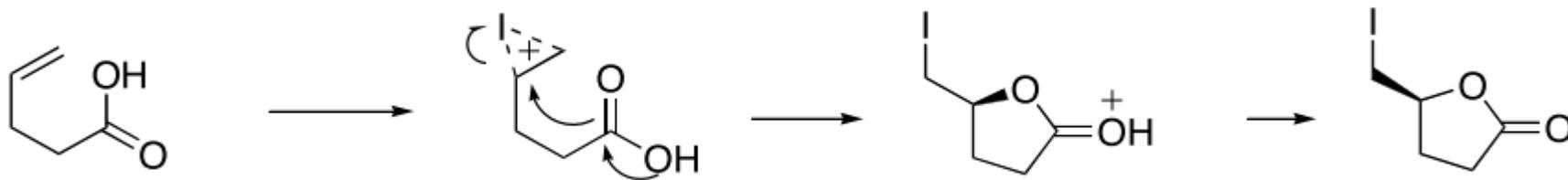
Bromação envolve um complexo com transferência de carga que colapsa num intermediário par iônico. O catião pode ser um carbocátion ou um bromônio



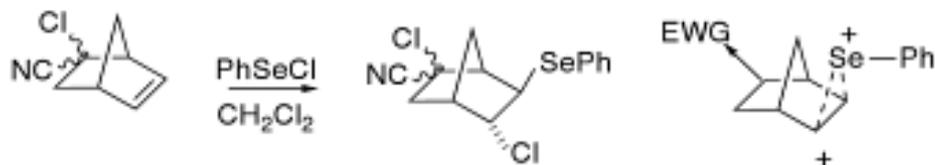
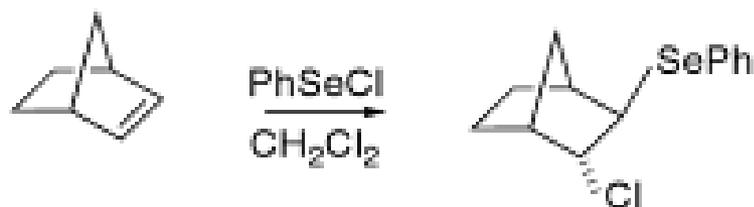
Com outros nucleófilos e com metais



Iodo lactonização preferência por anéis de 5 membros

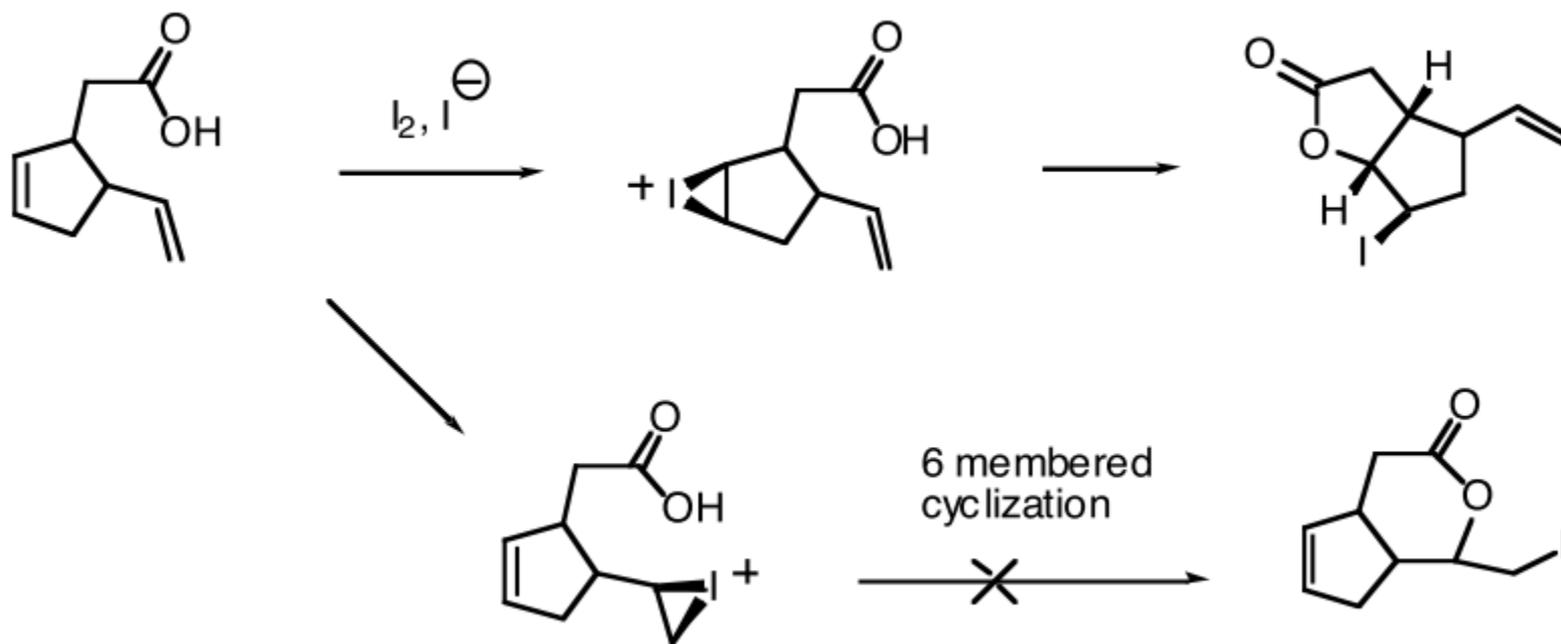


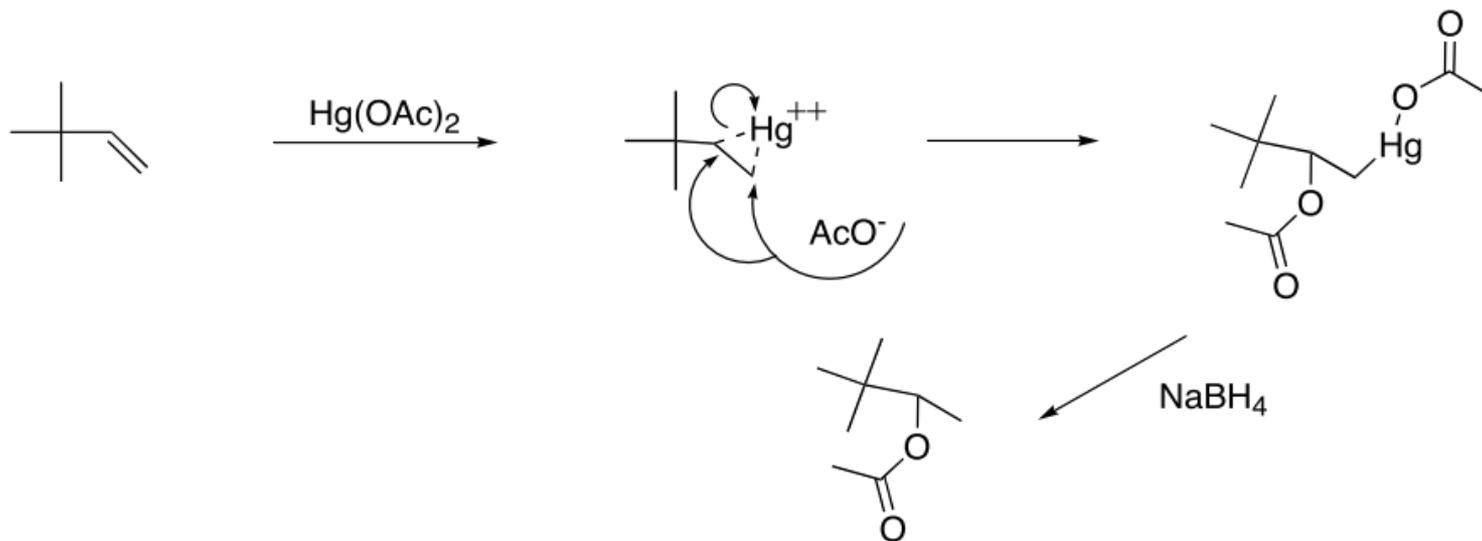
Reações com selenio dão produtos anti e produto Markovnikof



Ion seleniranion não simétrico e adição de cloreto é facilitada por grupos retiradores de eletrons

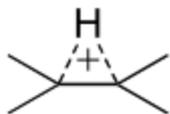
Preferencia por aneis de 5 miembros



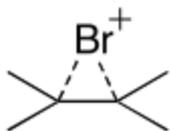


Markovnikoff regio e estereosseletividade

Comparação entre os intermediários cationicos em ponte

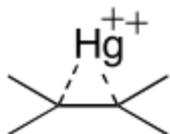


- a) H^+ é duro e não tem eletrons não compartilhados
- b) É carbocátion ou o cation em ponte é eletrodeficiente



- a) Br^+ é um ácido mole
- b) O íon bromônio pode ser representado com duas ligações covalentes

bromine



- a) Hg^{+2} é um ácido mole muito polarizável
- b) Tem uma estrutura em ponte eletrodeficiente

A. E1 Mechanism

First Order Kinetics: $\text{rate} = k[\text{RX}]$

LFER indicate cationic character of the TS

Strong dependence on leaving group

B. E2 Mechanism

Second Order Kinetics: $\text{rate} = k[\text{RX}][\text{base}]$

Leaving group effect is normally $\text{I} > \text{Br} > \text{Cl} \gg \text{F}$ because bond-breaking occurs in RDS.

Kinetic isotope effect for both β -C-H and leaving group.

Kinetic isotope effect for both α - and β -carbons.

C. E1cb(rev)

Second Order Kinetics: $\text{rate} = k[\text{RX}][\text{base}]$

Exchange of β -H with protic solvent

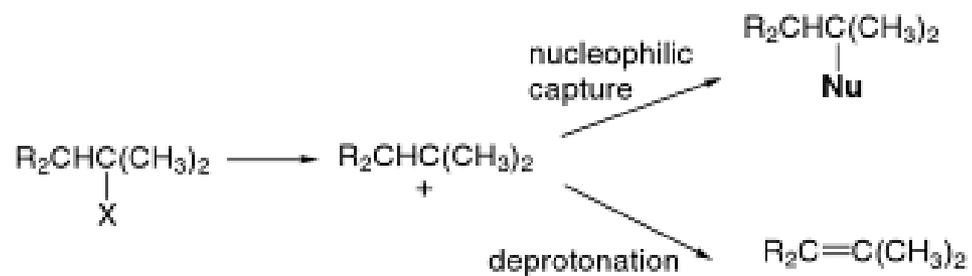
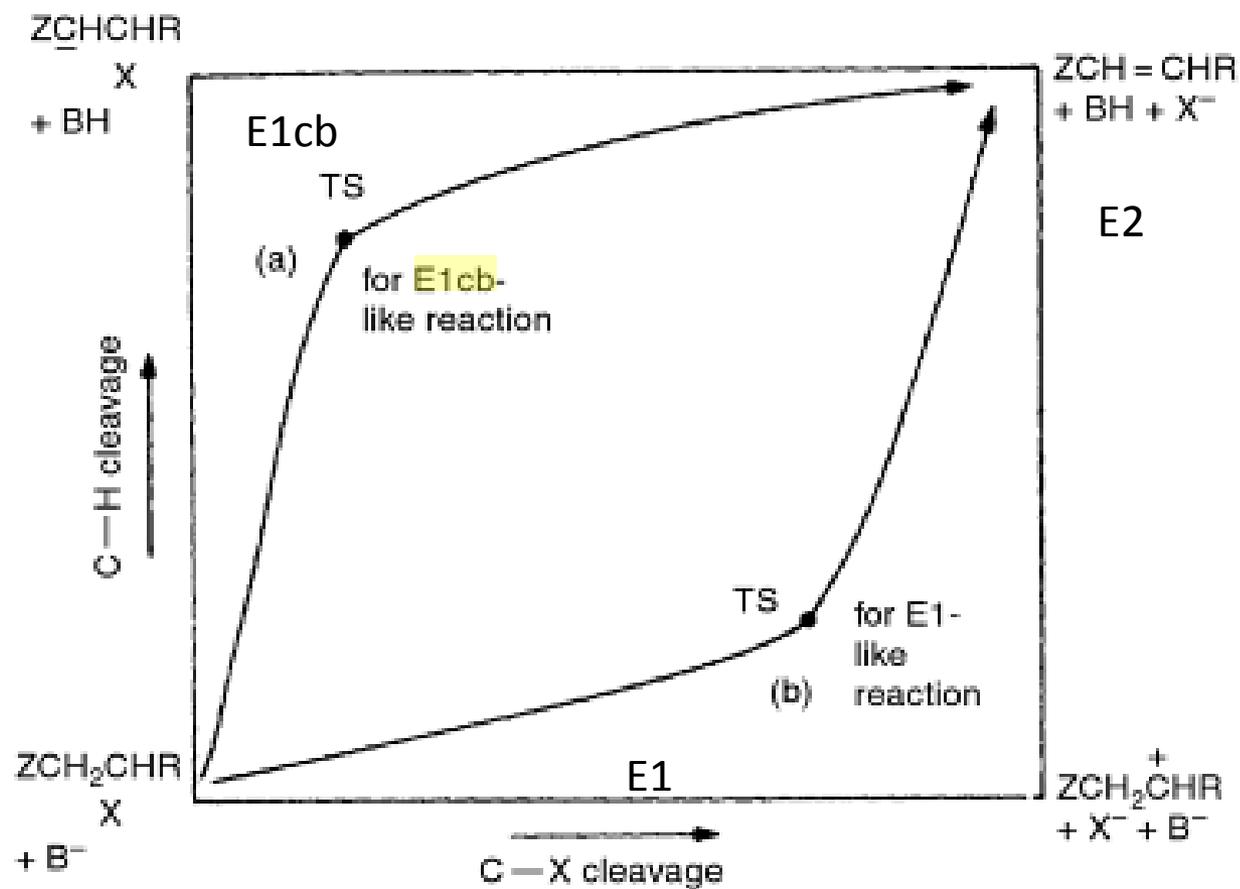
LFER indicate anionic character in TS

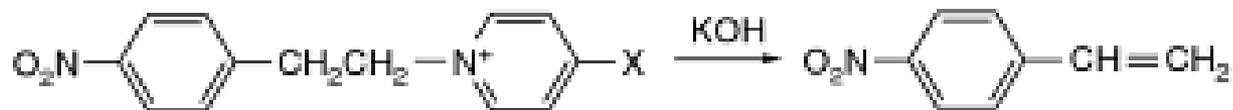
D. E1cb(irr)

Second Order Kinetics: $\text{rate} = k[\text{RX}][\text{base}]$

Leaving group effect may be $\text{F} > \text{Cl} > \text{Br} > \text{I}$, since C-X bond-breaking is not involved in RDS.

LFER indicates anionic character in TS

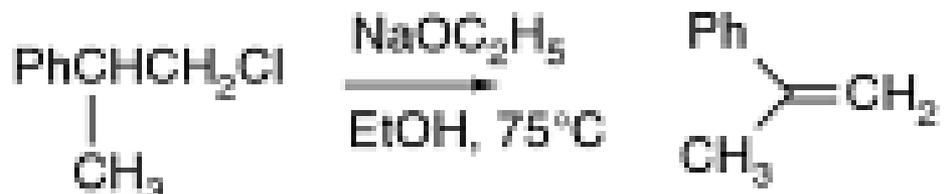




E1cb



E1Cb necessita de substituintes que estabilizam carbanion não é observado com haletos e sulfonatos simples e é mais possível de ser observado quando o grupo de saída é beta a um carbonil, nitro, ciano, sulfonil ou outro grupo estabilizante



E2 Baseado $k^{35}\text{Cl}/k^{37}\text{Cl} = 1,0059$ e $k\text{H}/k\text{D} = 5,37$ e $k\text{Br}/k\text{Cl} = 52$

A Change in the Rate-Determining Step in the E1cB Reactions of *N*-(2-(4-Nitrophenyl)ethyl)pyridinium Cations

John W. Bunting* and James P. Kanter

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. Received March 7, 1991

Abstract: Second-order rate constants have been measured (aqueous solution, $I = 1.0$, 25 °C) for the hydroxide ion catalyzed elimination reactions of 12 *N*-(2-(4-nitrophenyl)ethyl)pyridinium cations (**3**) bearing a variety of substituents in the pyridine ring. Brønsted plots as a function of the basicity of the pyridine leaving group are concave-down, which is consistent with a change in rate-determining step within an E1cB mechanism. These plots are characterized by $\beta_{lg} = -0.17$ for the rate-determining deprotonation for $pK_{BH} < 6.5$, and $\beta_{lg} = -0.39$ for the rate-determining expulsion of the pyridine nucleofuge from the carbanionic intermediate for $pK_{BH} > 6.5$. Elimination reactions in basic D₂O occur without any significant incorporation of deuterium into the 4-nitrostyrene product, and require the presence of a hydrogen-bonded carbanionic intermediate in which nucleofuge expulsion occurs faster than exchange of hydrogen-bonding water molecules. Rate-determining deprotonation in these elimination reactions occurs 50-fold more slowly than for the corresponding reactions of the *N*-[2-(4-nitrophenyl)ethyl]quinuclidinium cations that have also been reported to have $\beta_{lg} = -0.17$, but which do not show an analogous change in the rate-determining step upon variation of the nucleofuge basicity. The analogous elimination of the 1-methyl-3-[2-(4-nitrophenyl)ethyl]imidazolium cation occurs a further 30-fold more slowly than that predicted for **3** having a pyridine leaving group of the same basicity as 1-methylimidazole. The E1cB reactions of **3** are similar to the analogous reactions of *N*-(2-cyanoethyl)pyridinium cations (**1**) in displaying a change in the rate-determining step with nucleofuge basicity; however, the β_{lg} values for **1** and **3** are quite different for both k_1 and k_2/k_{-1} .