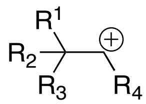
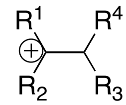
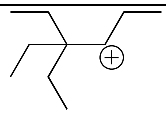
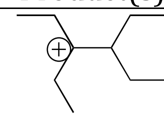
REACTION STUDY SHEET

NAME OF REACTION: **<u>Wagner-Meerwein (Vagner-Meerwein) Rearrangement of Carbocations</u>**

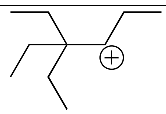
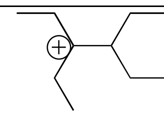
General form of the reaction:

Reactant	Reagent	Product(s)
	→	

A specific example

Reactant	Reagent	Product(s)
	→	

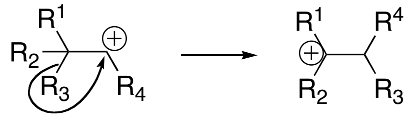
What ways can this specific example be asked on an exam (i.e. what flash cards do I need?)

	→	**?**
?	→	

What is the stereochemistry of this reaction? Since the empty 2p orbital of the carbocation is symmetrical on either side of the sp^2 carbocation carbon, we expect that migration of the alkyl group may occur with equal facility to either face of the carbocation. If this results in a new chiral center, we expect that the chiral center will be formed as a racemate unless there is already a chiral center present in the molecule.

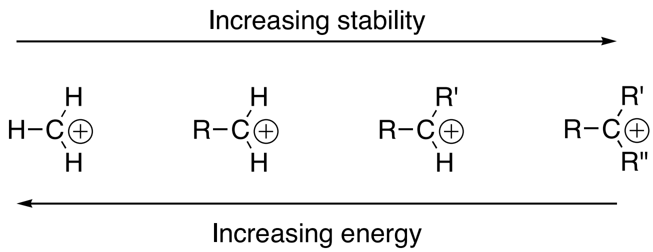
What is the regiochemistry of this reaction? The rearrangement is restricted to moving the migrating group *one atom distance only* (i.e. to the adjacent carbon atom). This means that only groups on the carbon atoms bonded directly to the carbocation carbon may migrate.

What is the mechanism of this reaction?

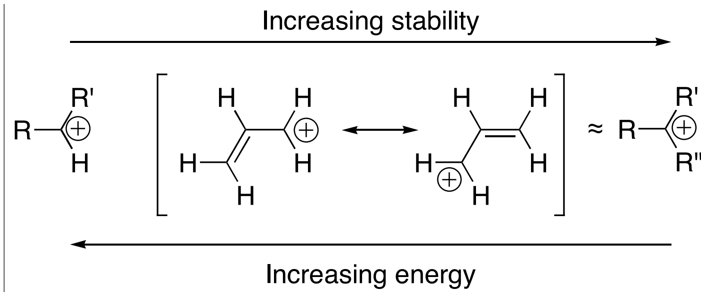


What is the driving force behind this reaction? A carbocation has one atom with a positive formal charge and an incomplete octet. The carbocation is stabilized by hyperconjugation with alkyl groups (which are weakly electron-releasing), or, better, by conjugation with the π bond of an alkene or an aromatic ring (which allows much better dispersal of the positive charge), or, even better, by a lone pair on an adjacent atom (which allows every atom in the cation to have a complete octet in the major resonance contributor.

Hyperconjugation leads to the generalization that tertiary (3°) carbocations are more stable than secondary (2°) carbocations, which are more stable than primary (1°) carbocations.

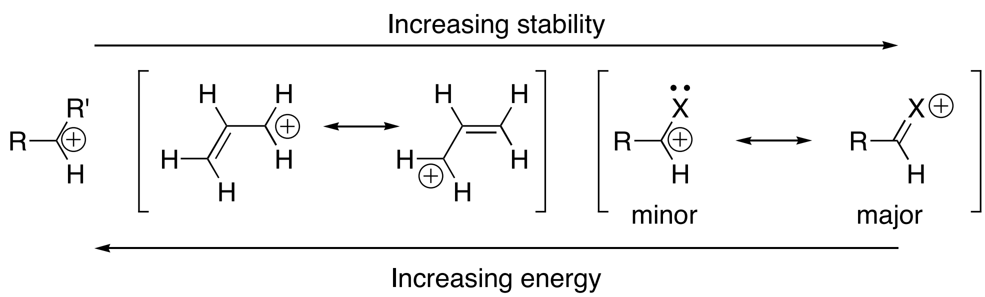


hyperconjugation



conjugation with a π bond

Conjugation with a π bond stabilizes a cation about as much as hyperconjugation with two additional alkyl groups. Tertiary allyl and benzyl cations are more stable than secondary allyl and benzyl cations, which are more stable than primary allyl and benzyl cations; primary allyl and benzyl cations are only slightly less stable than (actually, almost as stable as) a simple tertiary cation.



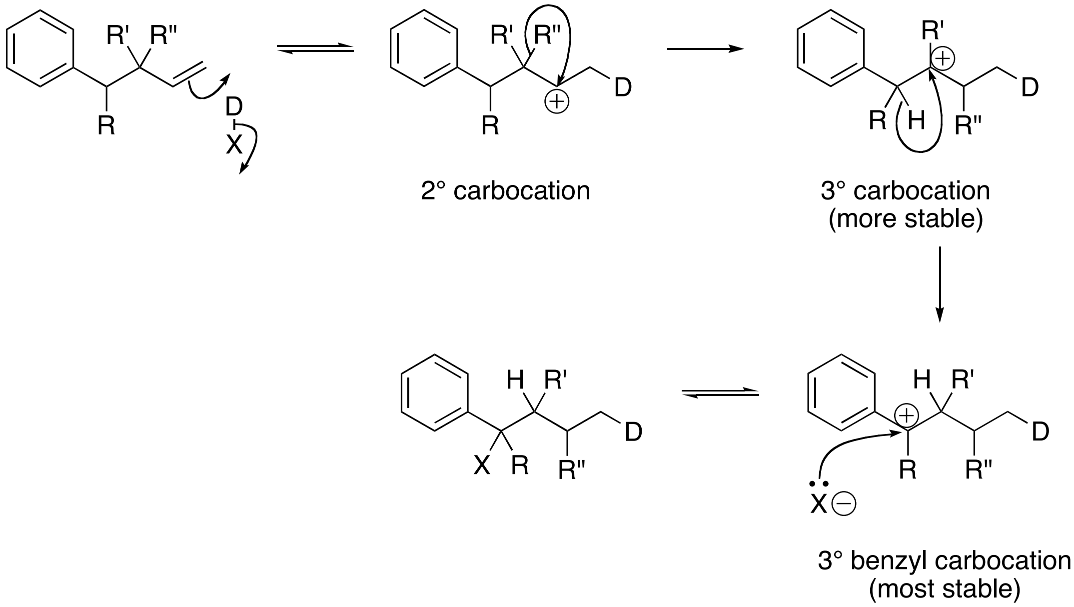
conjugation with a lone pair

Conjugation with a lone pair gives rise to a cation that has a major resonance contributor in which every atom has a compete octet. Such carbocations are the most stable of all, and are usually referred to as the heteronium ion (the major contributor to the resonance hybrid).

If a carbocation can give a more stable cation by a 1,2-, or Wagner-Meerwein (Vagner-Meerwein) rearrangement, it will do so very rapidly. Exothermic rearrangements are extremely fast, and typically require only milliseconds or microseconds to be complete. Rearrangements that are not exothermic are slow, taking minutes or hours for completion, and rearrangements that are endothermic do not occur (or take weeks for completion). *Exothermic rearrangements are not reversible*.

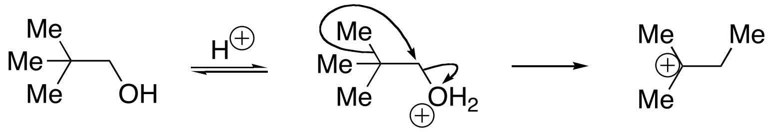
Exothermic rearrangements are extremely fast, and typically proceed to completion in only milliseconds or microseconds. Rearrangements that are not exothermic, but are close to thermoneutral (neither exothermic nor endothermic) are slow, taking minutes or hours for completion, and rearrangements that are endothermic do not occur (or take weeks for completion). *Exothermic rearrangements are not reversible*.

Wagner-Meerwein rearrangements are known where an alkyl group or hydrogen migrates; which group actually migrates often depends on the exact nature of the rearranging cation.



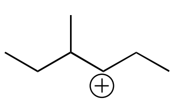
Other Aspects of the Reaction:

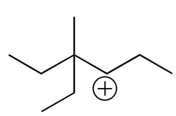
Wagner-Meerwein rearrangement often accompanies the loss of the leaving group during S_N1 reactions, especially if the leaving group is in a primary position adjacent to a quaternary center (a neopentyl-type system). This type of reaction is called **Neighboring Group Participation** or **Anchimeric Assistance**.

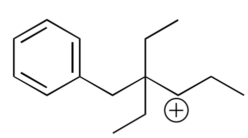


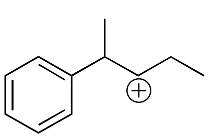
Practice Problems:

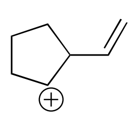
Will the following carbocations rearrange or not? If a cation will rearrange, give the structure of the product cation. If it will rearrange more than one time (a "cascade" rearrangement), give the structures of all carbocations that occur in the pathway to the final carbocation product. Draw both canonical forms of any carbocation that is resonance stabilized.

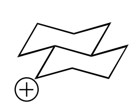
(a) 

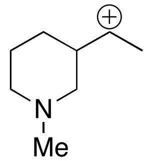
(b) 

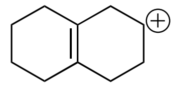
(c) 

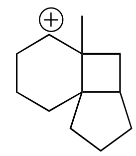
(d) 

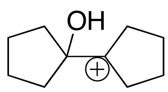
(e) 

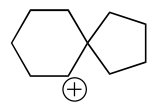
(f) 

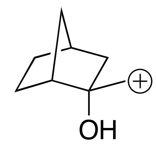
(g) 

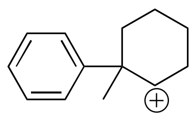
(h) 

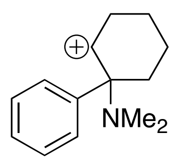
(i) 

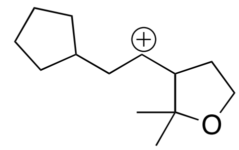
(j) 

(k) 

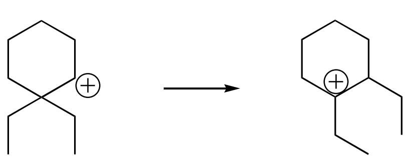
(l) 

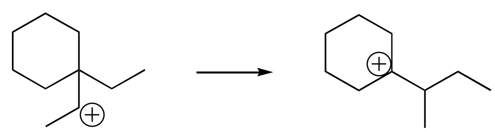
(m) 

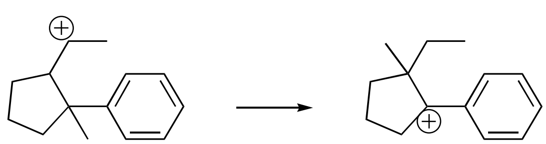
(n) 

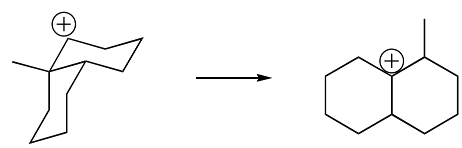
(o) 

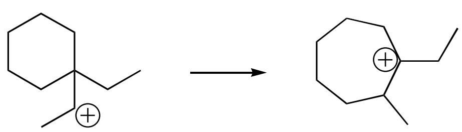
Draw a mechanism for each of the following transformations. Where more than one pathway is possible, give the structures of the other products that can be formed, and indicate if the product shown will be a major or minor product of the rearrangement.

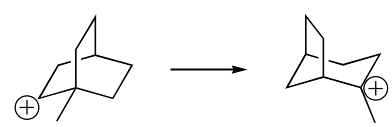
(a) 

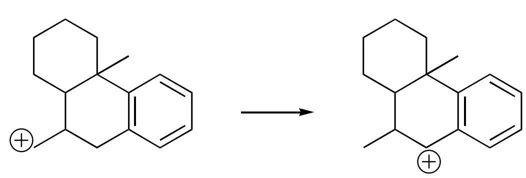
(b) 

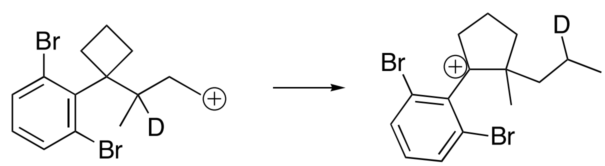
(c) 

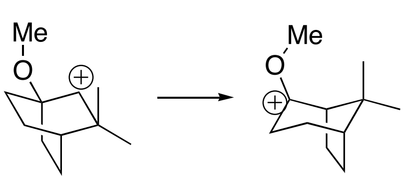
(d) 

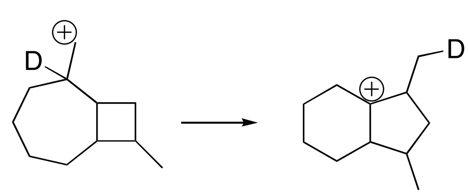
(e) 

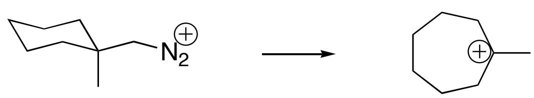
(f) 

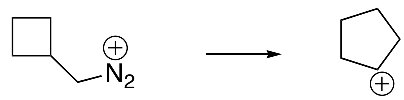
(g) 

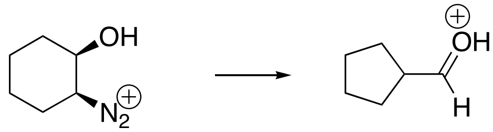
(h) 

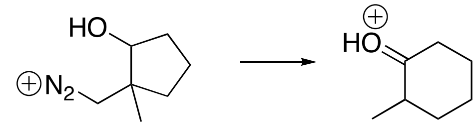
(i) 

(j) 

(k) 

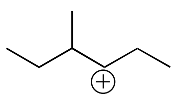
(l) 

(m) 

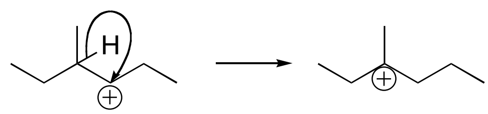
(n) 

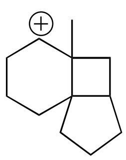
SELECTED ANSWERS

Will the following carbocations rearrange or not? If a cation will rearrange, give the structure of the product cation. If it will rearrange more than one time (a "cascade" rearrangement), give the structures of all carbocations that occur in the pathway to the final carbocation product. Draw both canonical forms of any carbocation that is resonance stabilized.

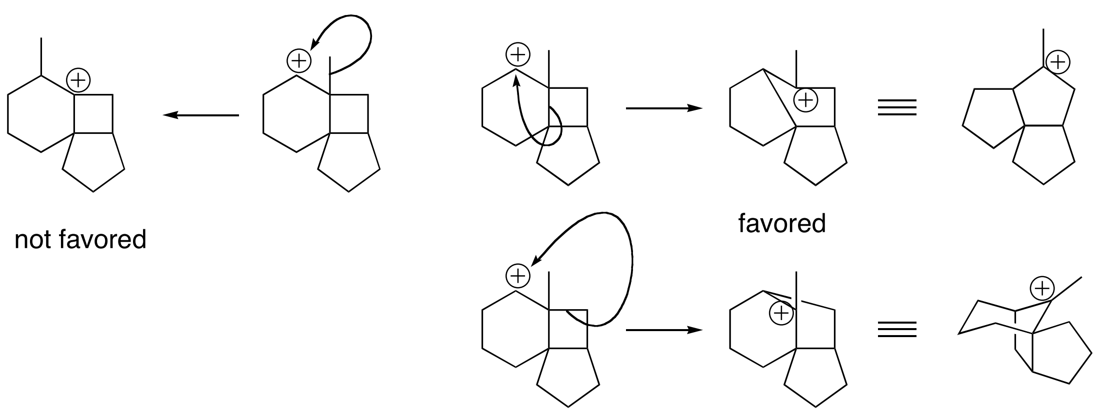


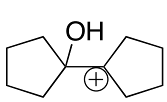
(a) This carbocation is secondary, and the migration of hydrogen (a hydride shift) will convert it to a tertiary carbocation. This is an exothermic reaction, so the rearrangement should occur rapidly.



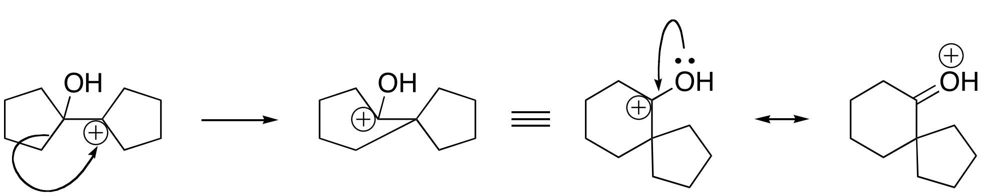


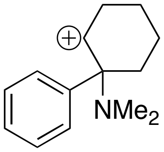
(i) This secondary carbocation has three possible rearrangements to a tertiary carbocation. In the rearrangement that is not favored, which involves the shift of a methyl group (a methide shift), the product carbocation retains the strained four-membered ring. In the favored rearrangements, which each involves the 1,2-shift of a ring bond to expand the four-membered ring to a five-membered ring, the product carbocation is much less strained. Whjich of these two favored carbocations is formed depends on the stereochemistry of the ring junctions of the starting secondary carbocation.



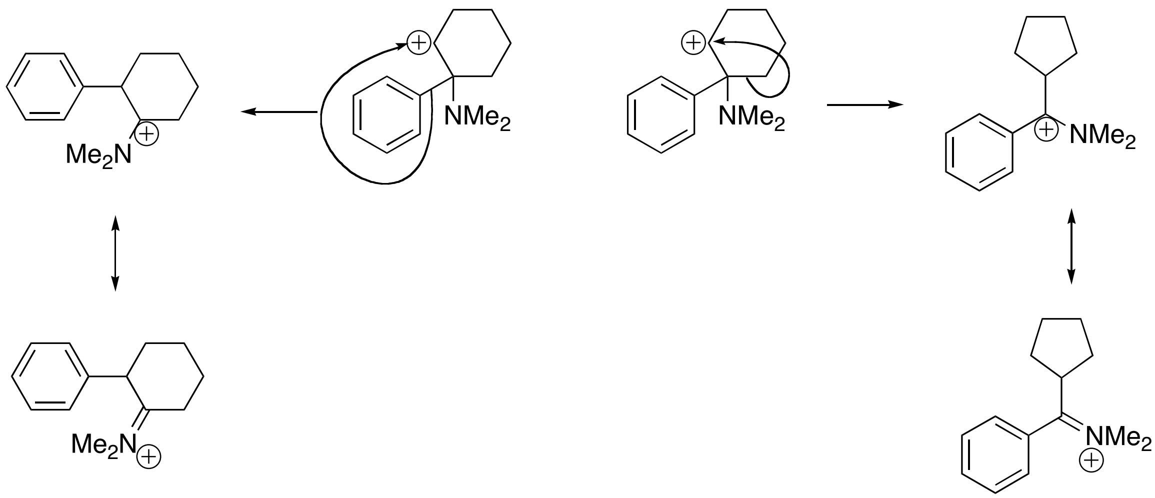


(j) Although it is tertiary, this tertiary carbocation will rearrange to the alternative cation with an oxygen atom directly bonded to the cation carbon. This allows the lone pair on oxygen to be used to stabilize the cation, and the major resonance contributor to the product cation is an oxonium ion with every atom having a complete outer-shell octet.

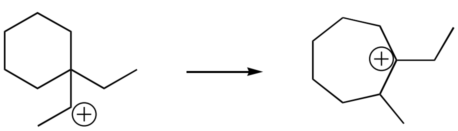




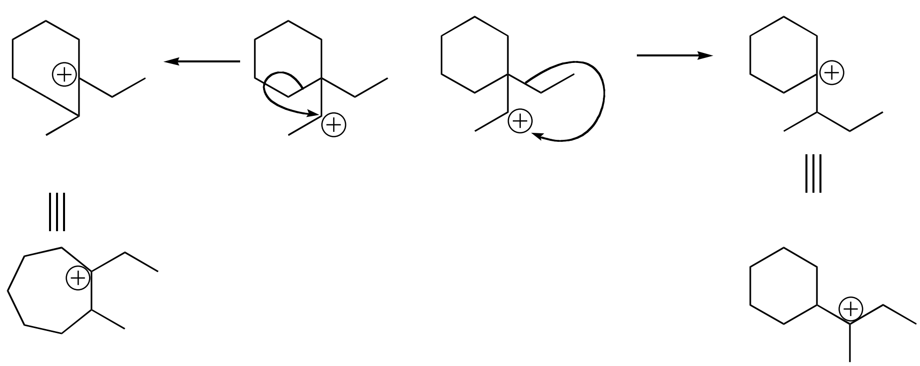
(n) This secondary carbocation can rearrange to two different carbocations that can be stabilized by the lone pair on the nitrogen atom. In both cations, the major contributor to the resonance hybrid is an iminium ion, in which every atom has a complete outer-shell octet. The right-hand ion is also conjugated with the aromatic ring, which makes this ion the more stable of the two.

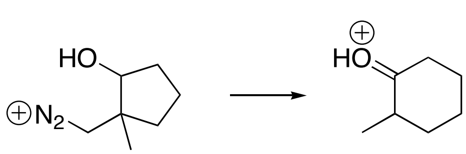


Draw a mechanism for each of the following transformations. Where more than one pathway is possible, give the structures of the other products that can be formed, and indicate if the product shown will be a major or minor product of the rearrangement.



(e) The starting cation is secondary, and there are two different carbon-carbon bonds that could rearrange, giving a tertiary carbocation. In one of these, the ethyl group migrates to give a tertiary cyclohexyl cation (shown as the right-hand option). In the other, one of the methylene groups of the cyclohexane ring (i.e. one of the cyclohexane ring bonds) migrates to give a tertiary carbocation with an expanded ring (a cycloheptane). It is difficult to say which of the two possible products is likely to be the major product, and both will probably be formed.





(n) The leaving group in this ion is molecular nitrogen, which makes this leaving group (the diazonium ion) one of the best known. It is a good enough leaving group to generate a primary carbocation. In this reaction, the loss of the leaving group is accompanied by migration of a ring methylene group to give a tertiary carbocation, which then undergoes a subsequent migration of hydrogen to give the resonance-stabilized oxonium ion. The alternative rearrangement of the methyl group is also likely to occur readi;ly, to give the isomeric compound with a five-membered ring rather than the six-membered ring. Both rearrangements are likely to be major reaction pathways for this diazonium ion.