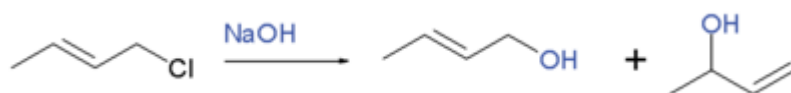


Allylic rearrangement

An **allylic rearrangement** or **allylic shift** is an organic reaction in which the double bond in an allyl chemical compound shifts to the next carbon atom. It is encountered in nucleophilic substitution.

In reaction conditions that favor a S_N1 reaction mechanism, the intermediate is a carbocation for which several resonance structures are possible. This explains the product distribution (or **product spread**) after recombination with nucleophile Y. This type of process is called an **S_N1' substitution**.

Alternatively, it is possible for nucleophile to attack directly at the allylic position, displacing the leaving group in a single step, in a process referred to as **S_N2' substitution**. This is likely in cases when the allyl compound is unhindered, and a strong nucleophile is used. The products will be similar to those seen with S_N1' substitution. Thus reaction of 1-chloro-2-butene with sodium hydroxide gives a mixture of 2-buten-1-ol and 3-buten-2-ol:



Nevertheless, the product in which the OH group is on the primary atom is minor. In the substitution of 1-chloro-3-methyl-2-butene, the secondary 2-methyl-3-buten-2-ol is produced in a yield of 85%, while that for the primary 3-methyl-2-buten-1-ol is 15%.

In one reaction mechanism the nucleophile attacks not directly at the electrophilic site but in a conjugate addition over the double bond:



This is usual in allylic compounds which have a bulky leaving group in S_N2 conditions or bulky non-leaving substituent which give rise to significant steric hindrance, thereby increasing the conjugate substitution. This kind of reaction is termed S_N1' or S_N2', depending on whether the reaction follows S_N1-like mechanism or S_N2-like mechanism. Similar to how there are S_N1' and S_N2' analogues for S_N1 and S_N2 reactions respectively, there also is an analogue for S_Ni, that being the S_Ni', applicable for reactions between allylic compounds and reagents like SOCl₂.

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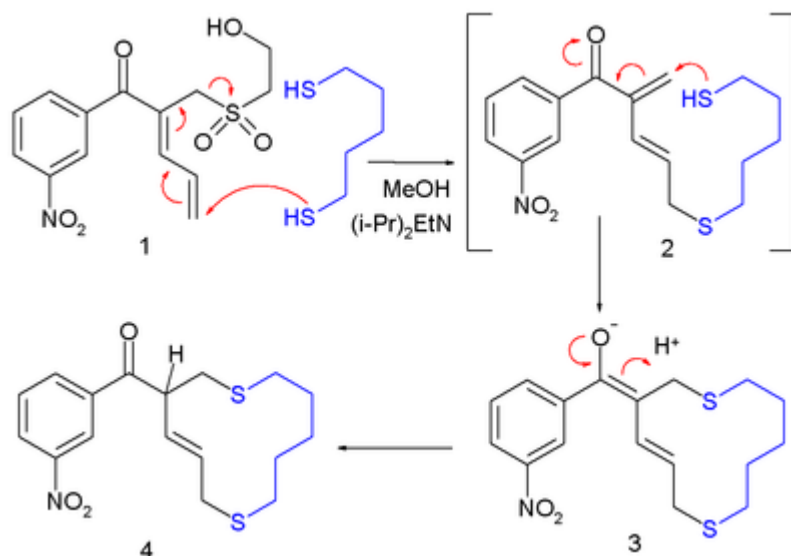
[S_N2' reduction](#)

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Scope

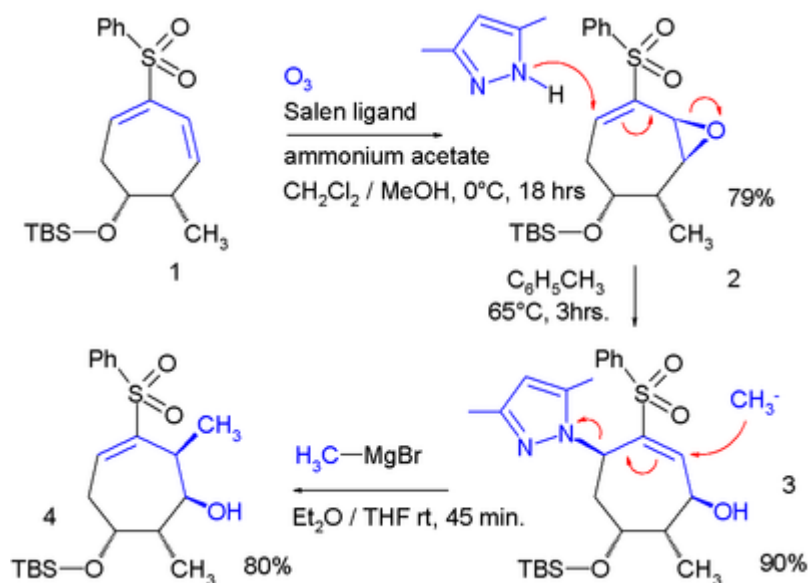
The synthetic utility can be extended to substitutions over butadiene bonds:^[1]



Reaction in methanol and catalyst diisopropylethylamine

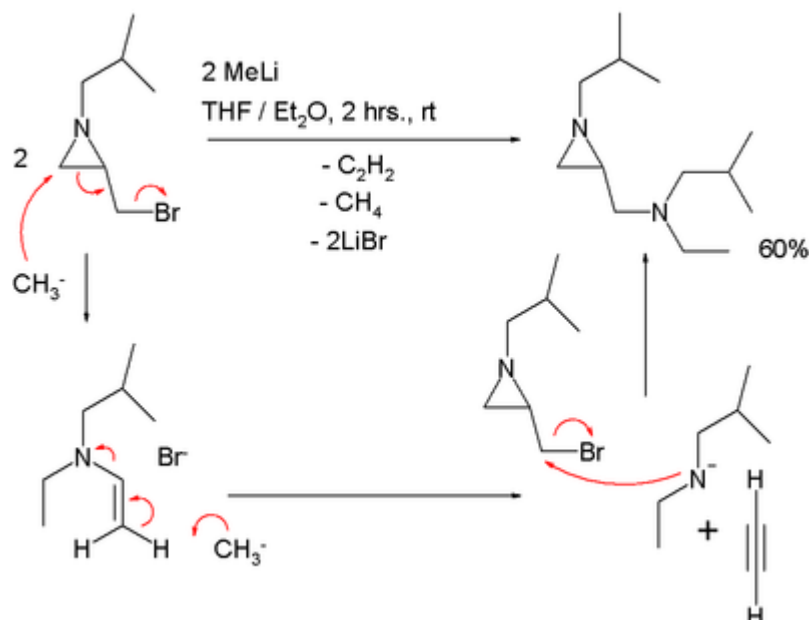
In the first step of this macrocyclization the thiol group in one end of 1,5-pentanedithiol reacts with the butadiene tail in **1** to the enone **2** in an allylic shift with a sulfone leaving group which reacts further with the other end in a conjugate addition reaction.

In one study^[2] the allylic shift was applied twice in a ring system:



In this reaction sequence a Jacobsen epoxidation adds an epoxy group to a diene which serves as the leaving group in reaction with the pyrazole nucleophile. The second nucleophile is methylmagnesium bromide expelling the pyrazole group.

An S_N2' reaction should explain the outcome of the reaction of an aziridine carrying a methylene bromide group with methylolithium.^[3]



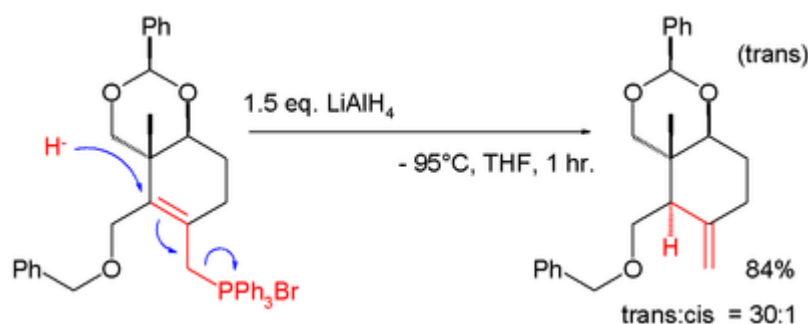
In this reaction one equivalent of acetylene is lost.

Examples of allylic shifts:

- Ferrier rearrangement
- Meyer–Schuster rearrangement

S_N2' reduction

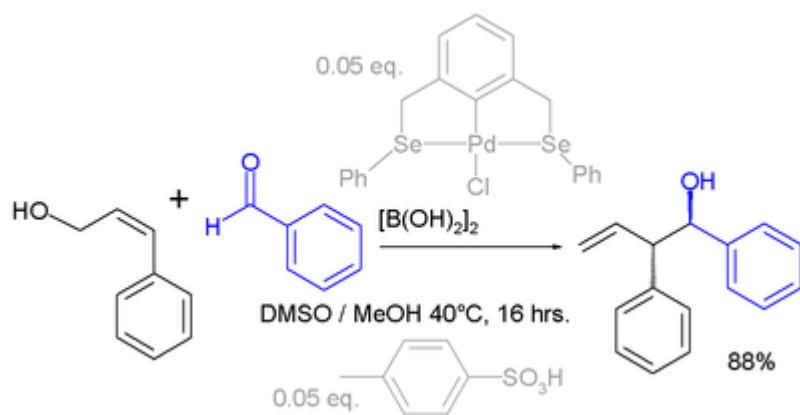
In one adaptation called a **S_N2' reduction** a formal organic reduction on an allyl group containing a good leaving group is accompanied by a rearrangement. One example of such reaction is found as part of a Taxol total synthesis (ring C):^[4]



The hydride is lithium aluminium hydride and the leaving group a phosphonium salt. The product contains a new exocyclic double bond. Only when the cyclohexane ring is properly substituted will the proton add in a trans position with respect to the adjacent methyl group. A conceptually related reaction is the Whiting reaction forming dienes.

Electrophilic allyl shifts

Allyl shifts can also take place with electrophiles. In the example below the carbonyl group in benzaldehyde is activated by diboronic acid prior to reaction with the allyl alcohol (see: Prins reaction):^{[5][6]}



References

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3. *Highly unusual conversion of 1-alkyl-2-(bromomethyl)aziridines into 1-alkyl-2-(N-alkyl-N-ethylaminomethyl)aziridines using methyl lithium* Matthias D'hooghe and Norbert De Kimpe *Chem. Commun.*, **2007**, 1275 - 1277, doi:10.1039/b616606g (<https://doi.org/10.1039%2Fb616606g>)
4. *Synthetic Studies on Taxol: Highly Stereoselective Construction of the Taxol C-Ring via SN2' Reduction of an Allylic Phosphonium Salt* Masayuki Utsugi, Masayuki Miyano, and Masahisa Nakada *Org. Lett.*; **2006**; 8(14) pp 2973 - 2976; (Letter) doi:10.1021/ol0608606 (<https://doi.org/10.1021%2Fol0608606>)
5. *Highly Selective and Robust Palladium-Catalyzed Carbon-Carbon Coupling between Allyl Alcohols and Aldehydes via Transient Allylboronic Acids* Nicklas Selander, Sara Sebelius, Cesar Estay, Kálmán J. Szabó *European Journal of Organic Chemistry* Volume **2006**, Issue 18, Pages 4085 - 4087 doi:10.1002/ejoc.200600530 (<https://doi.org/10.1002%2Fejoc.200600530>)
6. The active catalyst system in this reaction is a combination of a palladium pincer compound and p-toluenesulfonic acid, the reaction product is obtained as a single regioisomer and stereoisomer

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