

Chapter 5

Alkene Chemistry

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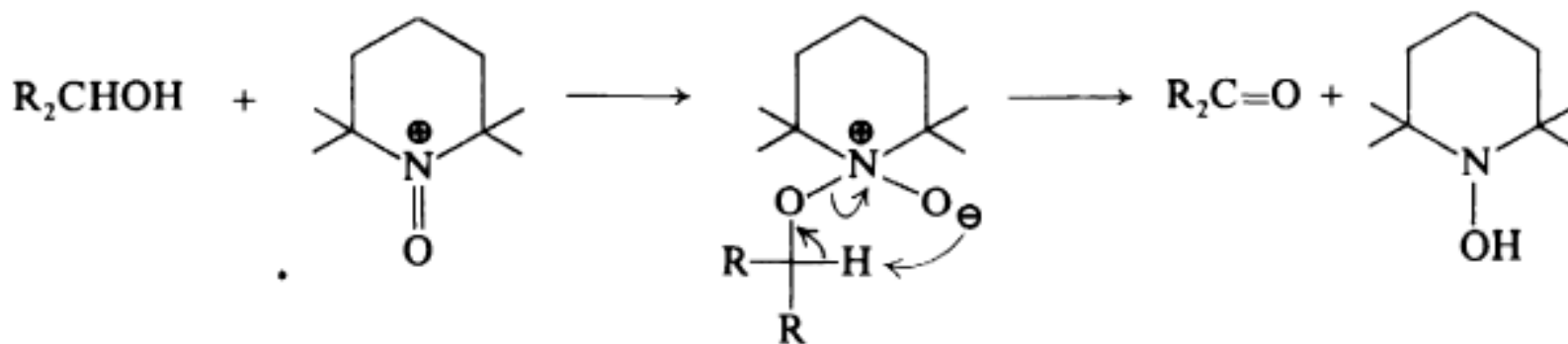
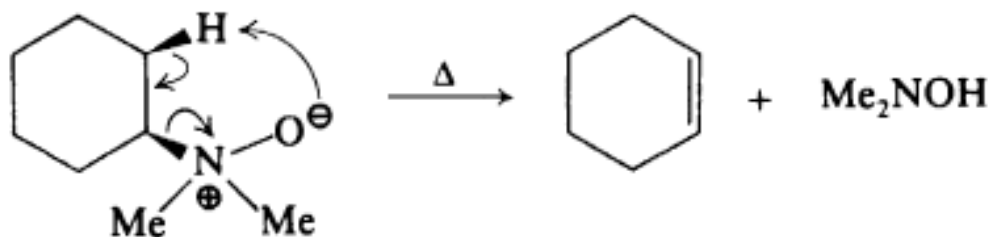
MISCELLANEOUS REACTIONS

FORMATION OF OLEFINIC LINKAGES BY ELIMINATION REACTIONS.

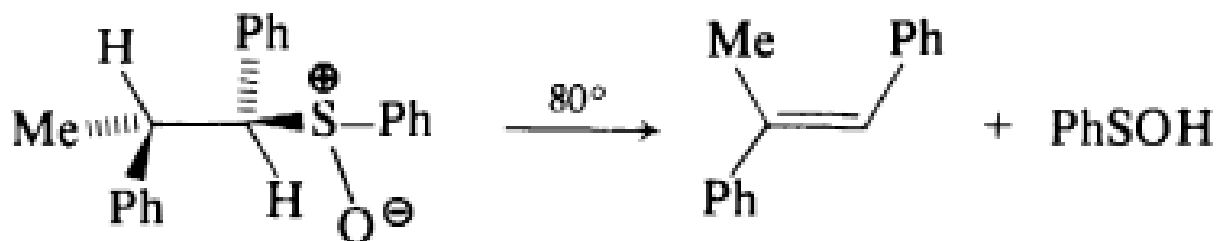
ELIMINATION vs. SUBSTITUTION

The most well-known method for double-bond formation is β elimination. In a pyrolytic elimination neither a base nor a solvent is needed. The nucleofugal group acts as an internal base in a cyclic E mechanism leading to cis elimination.

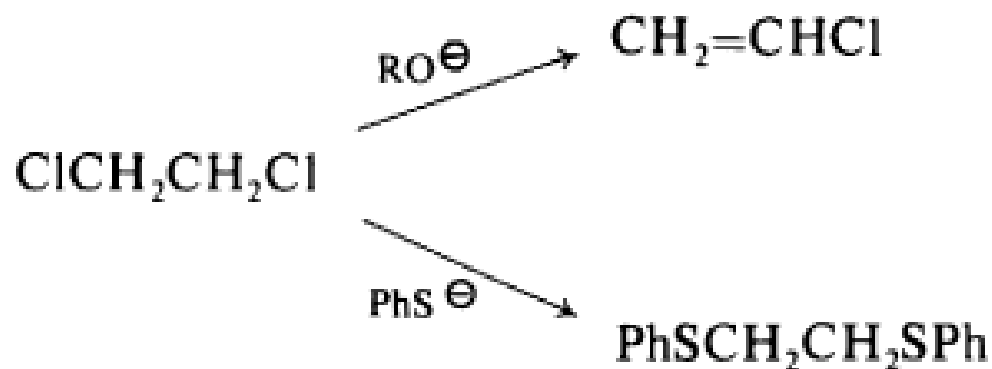
The Cope elimination demands lower temperatures than the Hofmann degradation. This is presumably due to the hardness of the oxygen base which is further augmented by the neighboring nitrogen. The oxidation of secondary alcohols by nitrosonium ion which is shown below could involve a *Cope type elimination*.



The thermolysis of sulfoxides has gained prominence as a technique for olefin synthesis because of the mild conditions required.



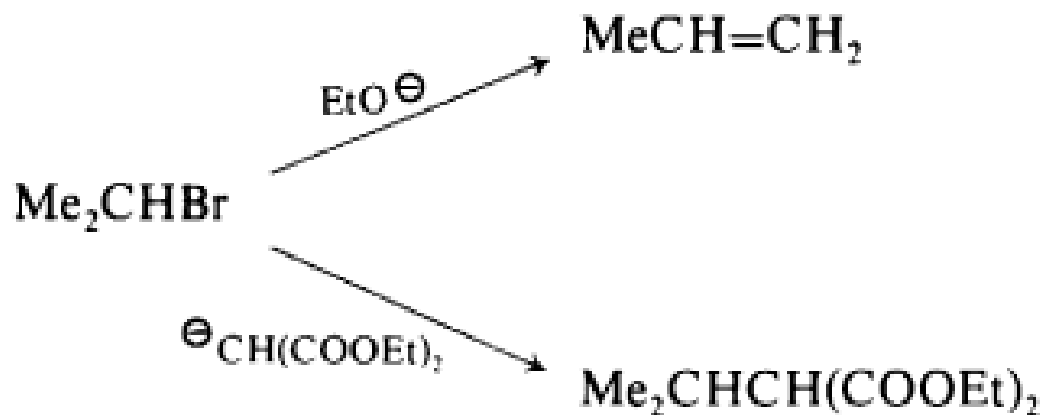
Treatment of alkyl halides with bases can lead to alkenes or substitution products, or both. Hard bases always favor elimination (by attacking the hard β proton), whereas soft donors prefer S_N2 displacement.

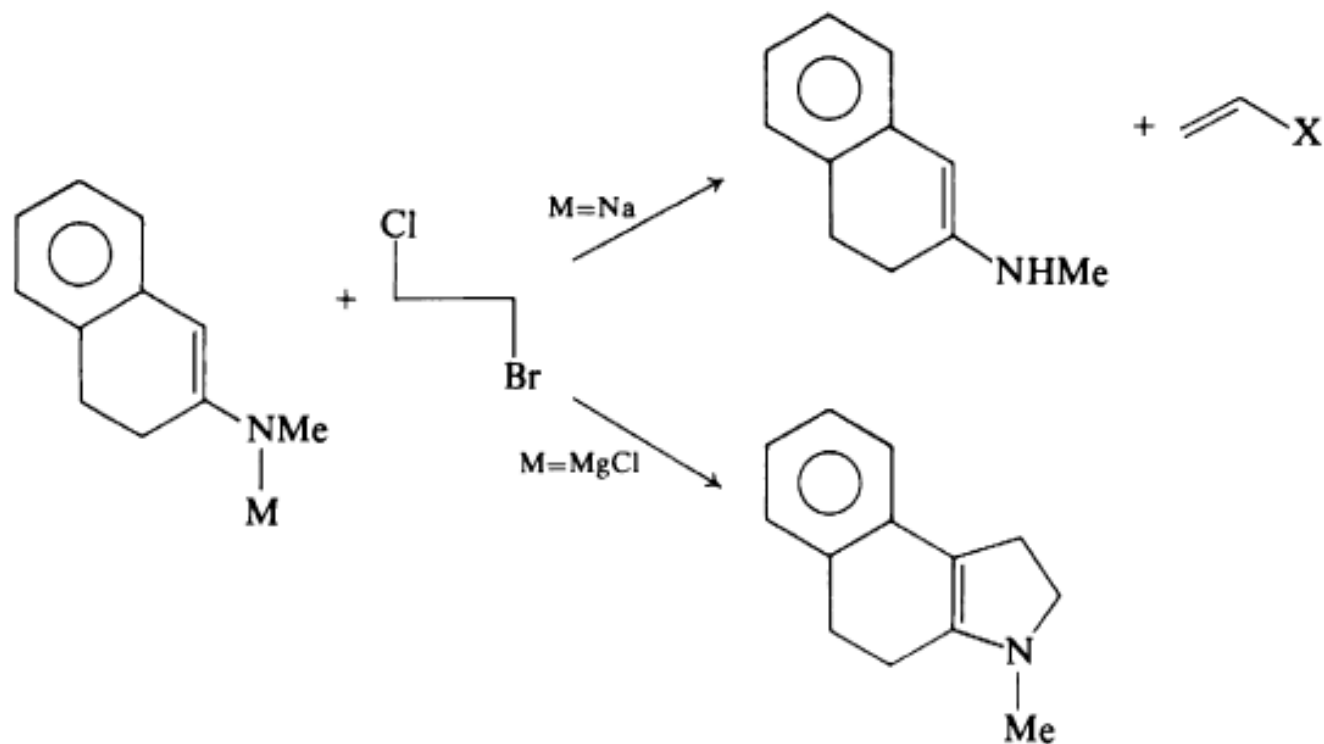


Halide ions, especially F^- , are weak bases in aqueous solution. However, in dry aprotic solvents $Et_4N^+F^-$ effectively induces elimination of HBr from 2-bromoethylbenzene. The ammonium chloride and bromide only promote halogen exchange.

At 80 °C, the fluoride decomposes into Et_3N , HF, and ethylene, thus demonstrating the high protophilicity of the hard fluoride ion.

Ethoxide and malonate anions have virtually identical proton basicity, but significantly different hardness. As a consequence, ethoxide promotes elimination of 2-bromopropane, whereas malonate effects substitution.





A change in the counter cation sometimes has profound influence on the reaction course. *N*-Sodio-2-methylamino-3,4-dihydronaphthalene induces dehydrohalogenation of 1,2-bromochloroethane, whereas the softer chloromagnesium salt of the same enamine leads to a displacement process.

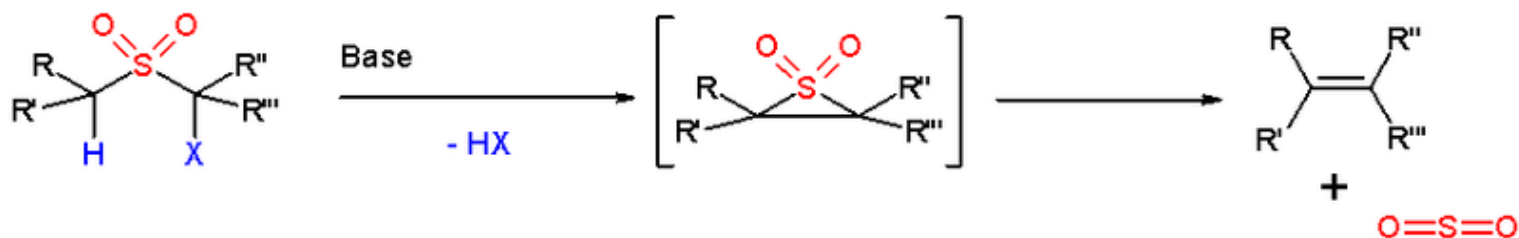
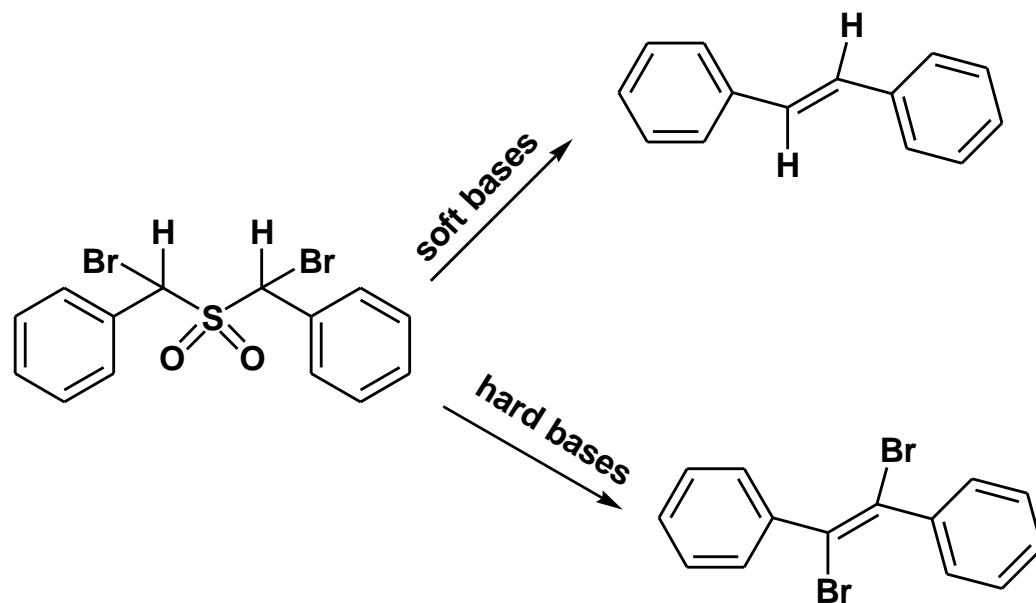
The dramatic increase in the E_2/S_N2 ratio in the reactions of tosylates with oxalate vs. formate anions has been ascribed to a possible bidentate attack on hydrogen by the oxalate ion . It should be noted that oxalate is a harder base compared to the formate.

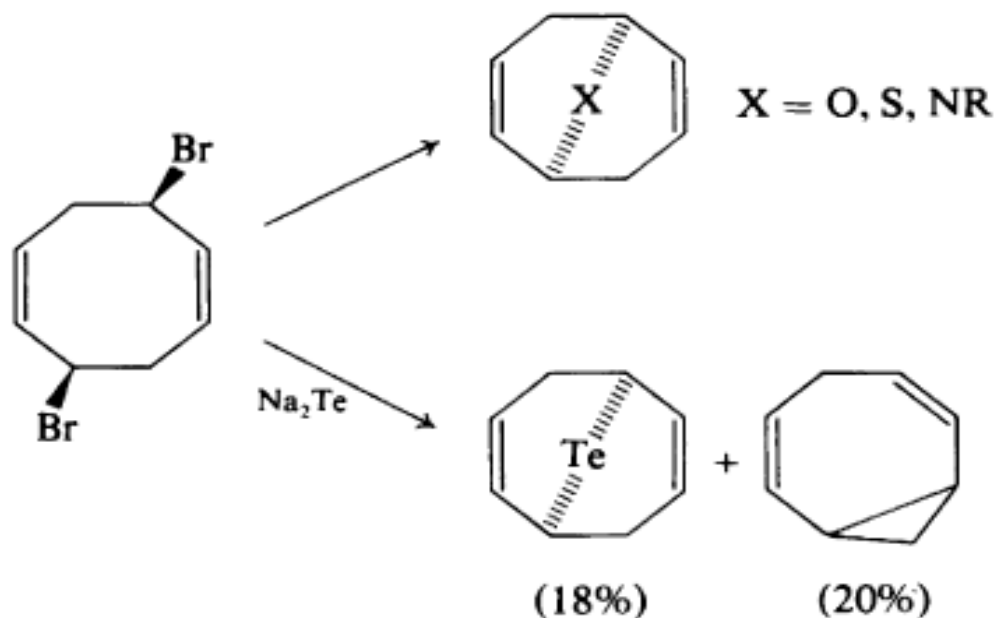
The concerted elimination of vicinal dihalides, in particular, dibromides, may be accomplished by a variety of reagents. Both iodide ion and zinc dust which are soft bases are efficient.

The relative halophilicity of trivalent phosphorus compounds, $n\text{-Bu}_3\text{P} > \text{Ph}_3\text{P} > (\text{EtO})_3\text{P}$, has been demonstrated from their reactions with *vic*-dibromides. Their reactivity parallel the softness of the central phosphorus atoms.

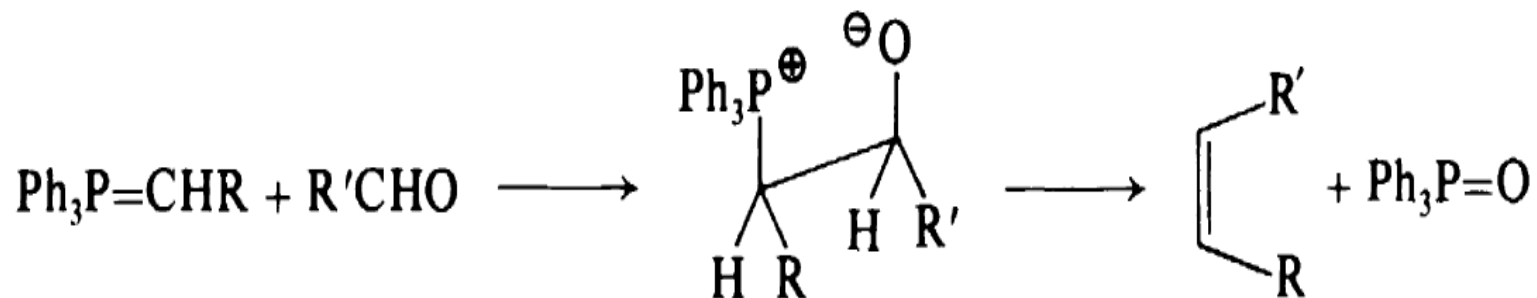
The debromination and dehydrobromination of *meso*- and *dl*-stilbene dibromides in dimethylformamide (DMF) have been scrutinized. The protophilicity and bromophilicity of the reagents, $F^- > Cl^- > DMF$ and $I^- > Br^- > Cl^- > Sn^{2+} > DMF$, respectively, are in accordance with the hard and soft scales.

In the 1,3-elimination of bis- α -bromobenzyl sulfones, soft bases (PhS^- , I^- , H^- , Ph_3P , Mg , Zn) attack the bromine atom to give stilbenes as the final products, whereas hard bases (MeO^- , R_3N , DMF, dimethylacetamide) abstract an α -hydrogen which leads to bromostilbenes (*Ramberg-Bäcklund reaction*).





Although 9-heterabicyclo[3.3.1]nona-2,6-dienes are the sole products from the double displacement of (Z,Z)-cis-3,7-dibromocycloocta-1,5-diene with oxygen, nitrogen, and sulfur bases, the very soft sodium telluride also effects a concurrent cycloelimination.



The popular *Wittig reaction* is a condensative elimination which is especially valuable for the preparation of (*Z*)-olefins under salt-free conditions.

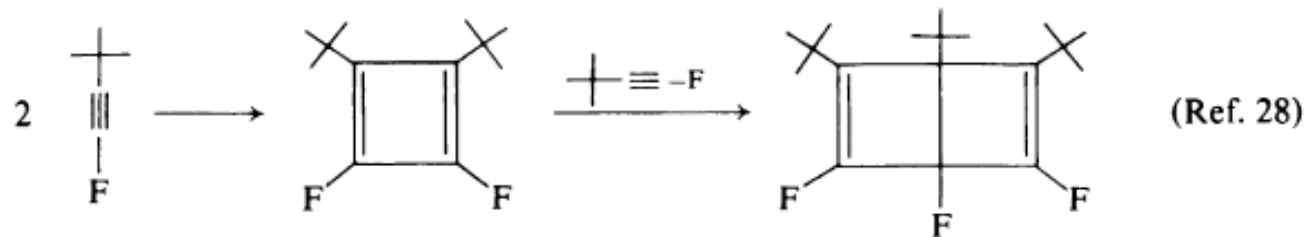
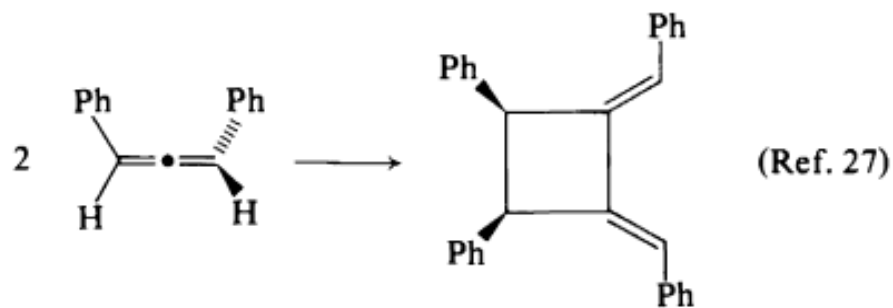
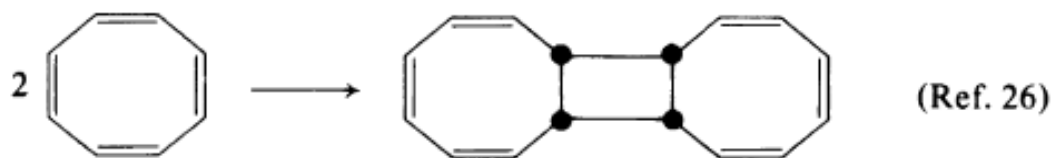
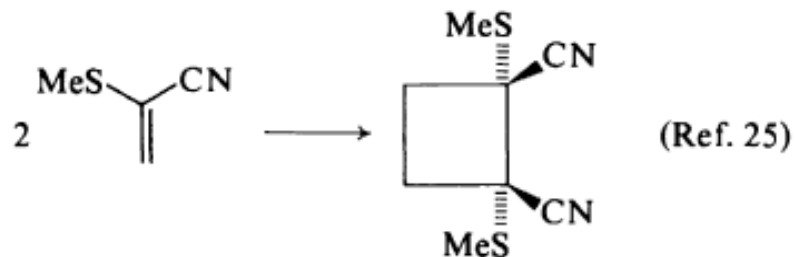
ADDITION TO DOUBLE BONDS

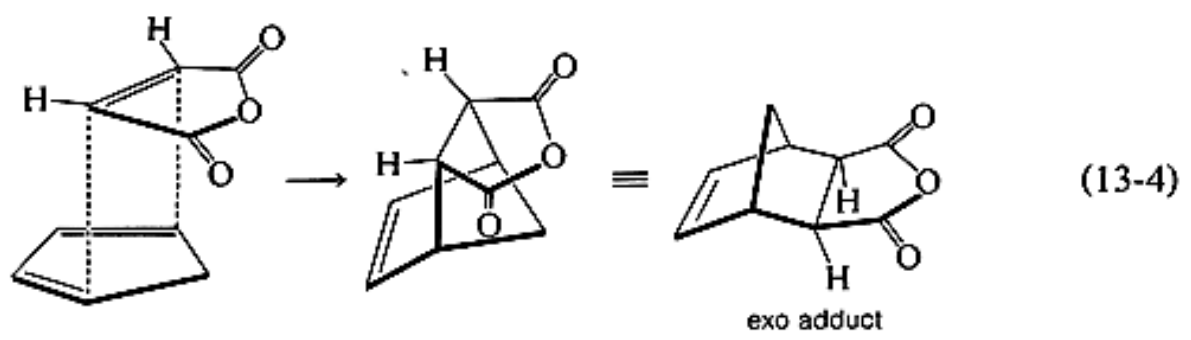
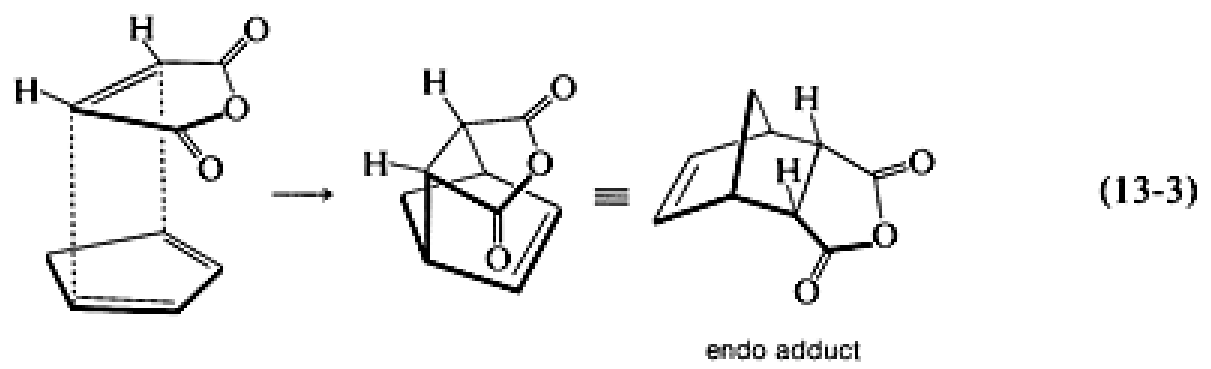
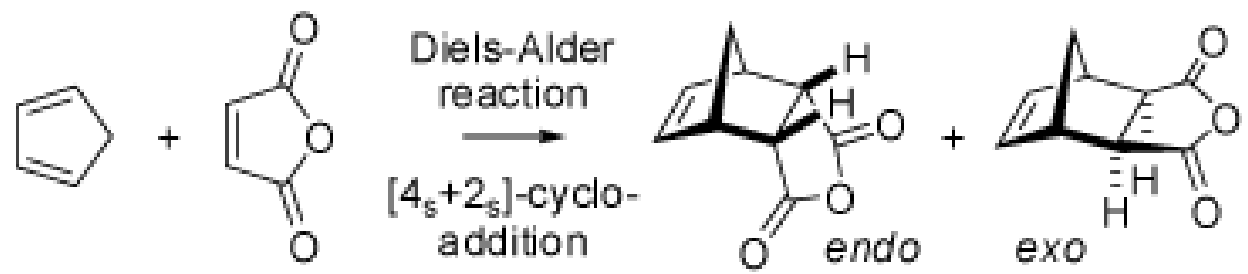
HOMOPOLAR ADDITION:

Olefins are essentially soft donors, π Complexation of alkenes with soft metal ions, such as Ag^+ , Pt^{4+} , and Pd^{2+} , is well established. The addition of halogens and pseudohalogens is commonly regarded as proceeding via the π complexes, as detected spectroscopically for the olefin-bromine charge transfer Species.

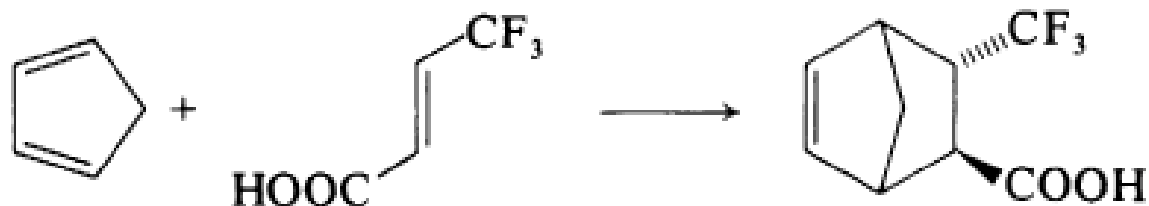
Alkenes may undergo uncatalyzed dimerization which, according to the Woodward-Hoffmann rules, is nonconcerted. The salient feature is that the major products are often contrathermodynamic.

Homopolar Additions:

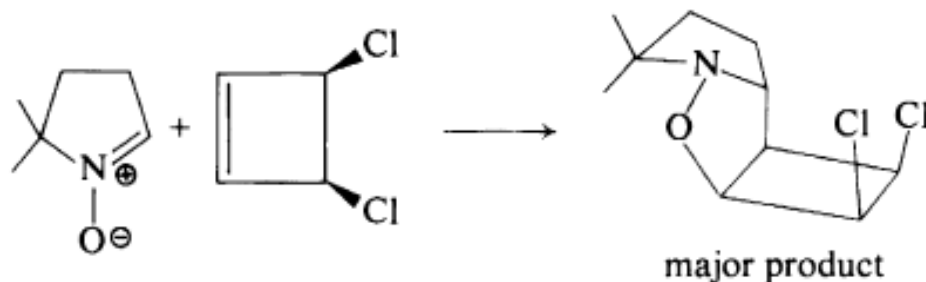




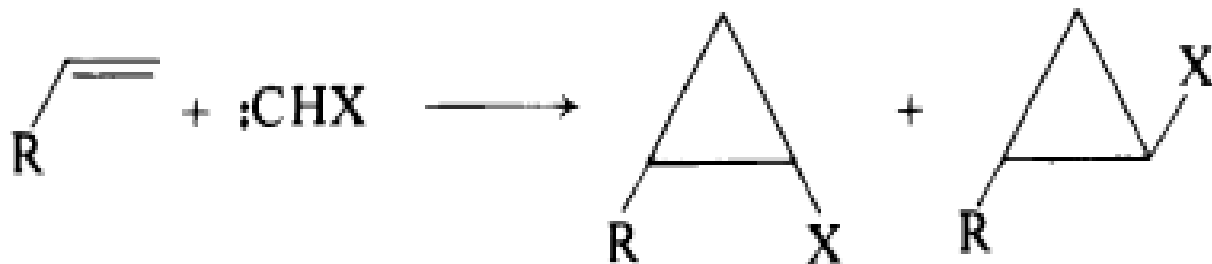
Cases which still obey the endo rule are known where direct π interactions are absent.



Selective 1,3-dipolar additions leading to the more crowded stereoisomers are also known, for example:



Carbene addition to olefinic linkages to form cyclopropanes also shows stereoselectivity. The cis compounds are the principal or exclusive adducts when X = alkyl, aryl, halo, alkylthio, or alkylseleno group, while the trans adducts are formed preferentially when X = trimethylsilyl, alkoxy-carbonyl, or aryloxy. It is clear that carbenes containing a soft substituent X prefer the reaction path leading to products in which X and alkyl R are closer, and the opposite is true when X is hard.



HETEROPOLAR ADDITION

The ionic addition of unsymmetrical addends to alkenes obeys the Markovnikov rule. For the addition of HX, the Markovnikov transition state of C-H bond formation is encouraged by symbiosis.

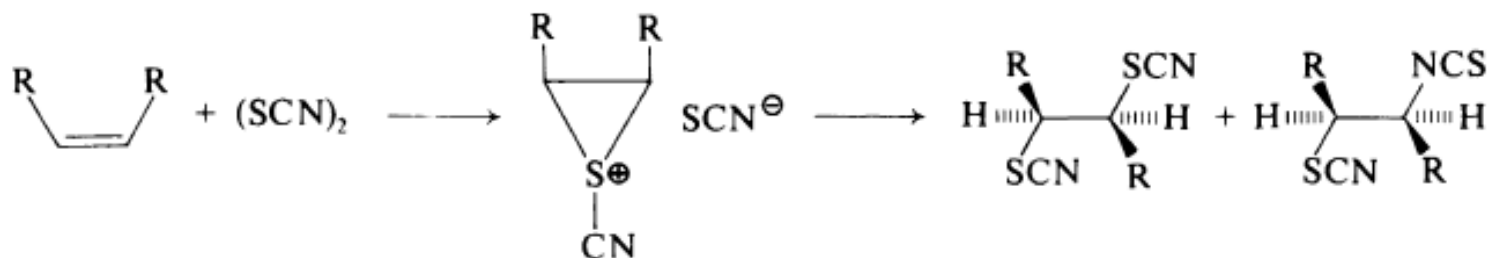
The creation of a more highly substituted carbocation is favored because the central carbon carries fewer soft hydrogen atoms. The carbenium ion may also be considered as an acid-base complex of a carbene-cation in which the carbene is a donor.



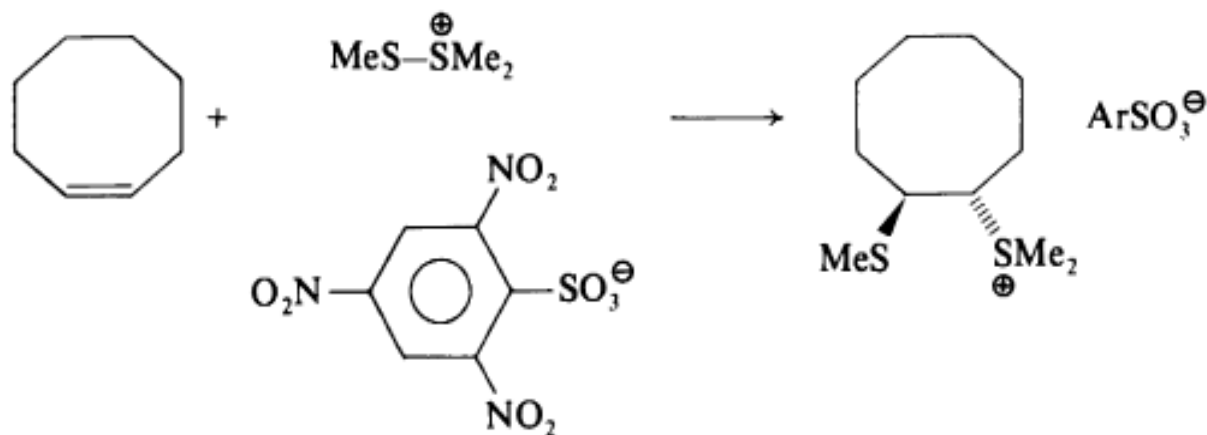
Thus, the secondary carbenium ion R_2CH^+ is made up of a resonance hybrid $R_2C:\rightarrow H^+ \leftrightarrow HRC:\rightarrow R^+ \leftrightarrow R^+ \leftarrow :CHR$, and the primary ion RCH_2^+ is represented by the hybrid of $HRC:\rightarrow H^+ \leftrightarrow H^+ \leftarrow :CHR \leftrightarrow H_2C:\rightarrow R^+$.

The major difference in the two arises from the relative viability of $HRC:\rightarrow R^+$ vs. $HRC:\rightarrow H^+$. The former is the more stable because R^+ is softer than H^+ and interacts better with the soft carbene.

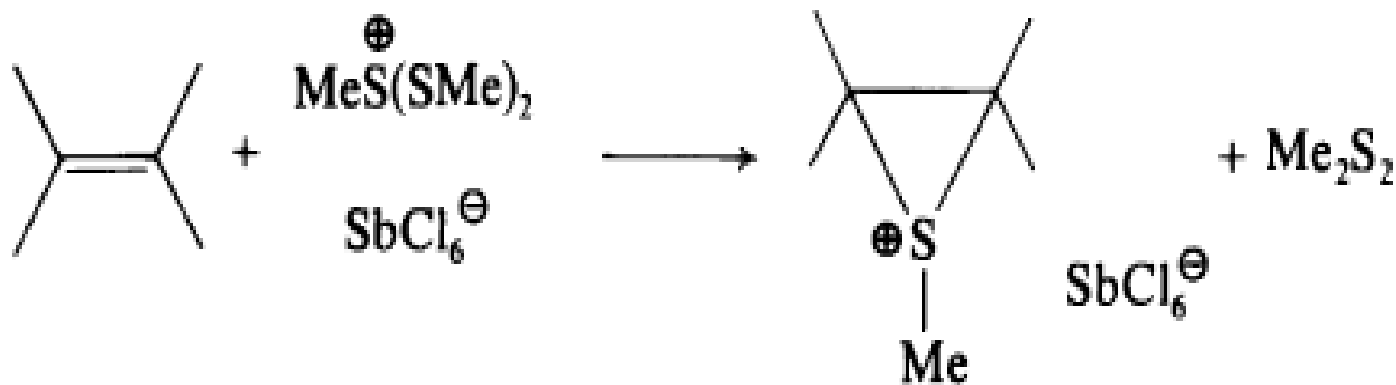
An ionic route is followed during addition of thiocyanogen to olefins. It seems likely that cyanoepisulfonium ions are the intermediates.



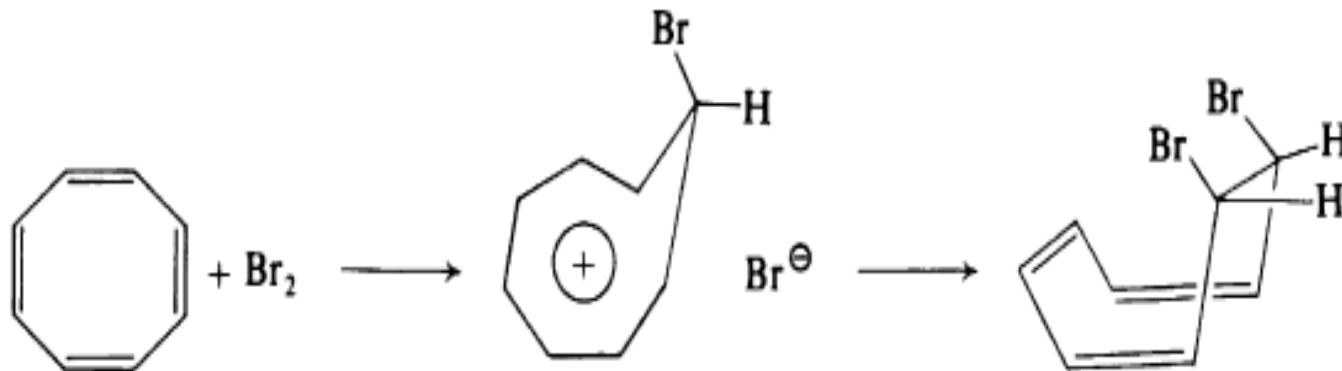
Dialkyl(alkylthio)sulfonium salts add across carbon-carbon double and triple bonds in a trans-stereospecific manner.



Episulfonium salts are conveniently prepared by treatment of olefins with methyl(bismethylthio)sulfonium hexachloroantimonate. The displacement by olefin must occur at the softer sulfur atom, although it is impossible to ascertain whether the double bond attacks the sulfonium center in the reaction described by Helmkamp *et al.*

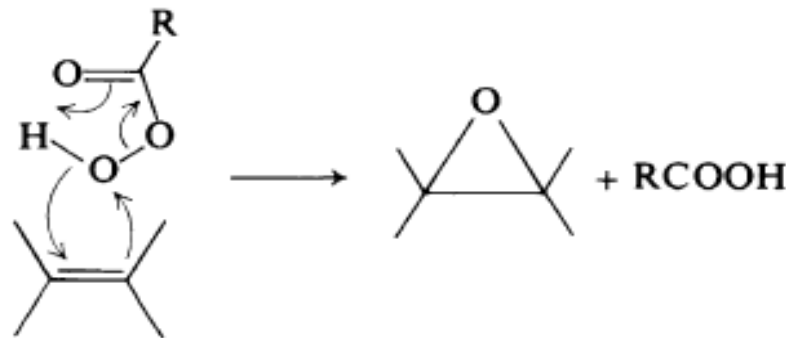


The addition of bromine to cyclooctatetraene at -55° generates a stable, nonclassical homotropylium ion which is subsequently captured by Br^- stereospecifically. The seemingly disconcerting fact is that both bromine atoms approach the olefin from the more hindered face yielding the less stable product.

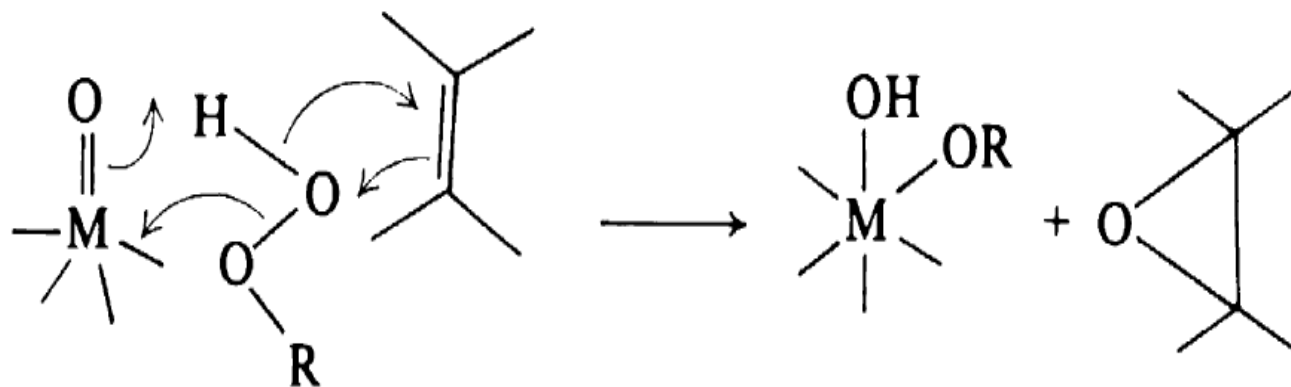


OXIDATION

The intrinsic instability of peracids caused by the soft-hard combination spurs the transfer of an active oxygen to soft bases.

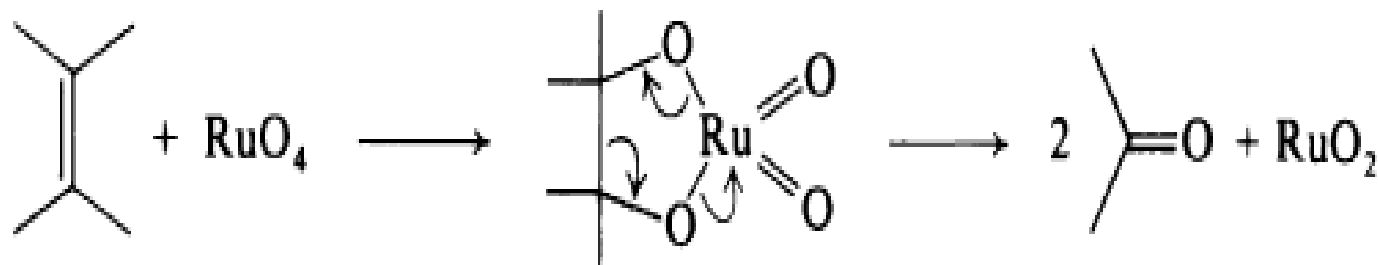


The metal ion-catalyzed decomposition of alkyl hydroperoxides in the presence of olefins also leads to the formation of oxiranes. The effectiveness of Mo(VI), Ti(IV), and W(VI) complexes is related to their being hard Lewis acids.

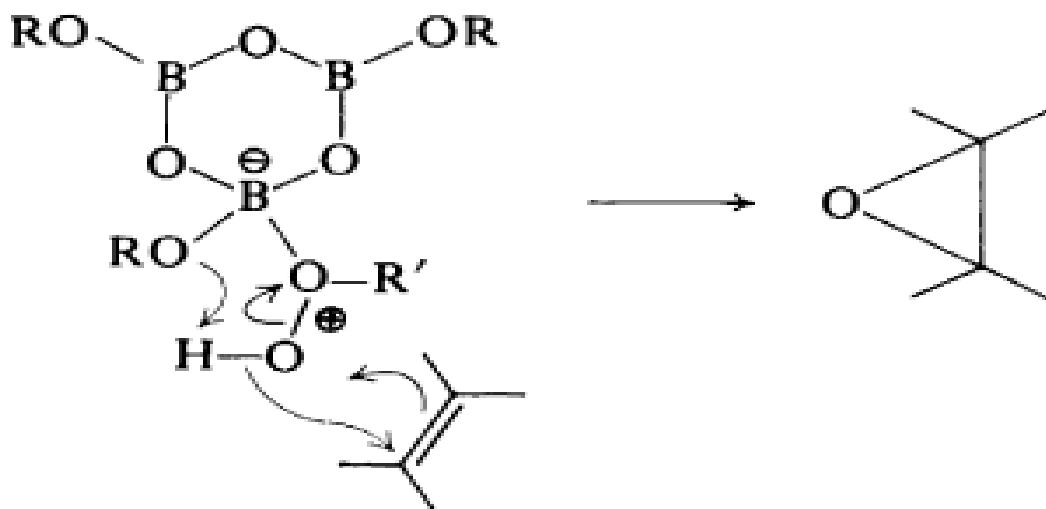


Mo(VI), Ti(IV), and W(VI)

Ruthenium tetroxide is an even more powerful oxidant for carbon-carbon double-bond cleavage. The escalated reactivity and the lessened stability of RuO_4 are the results of the softer metal atom being surrounded by hard oxygen atoms.

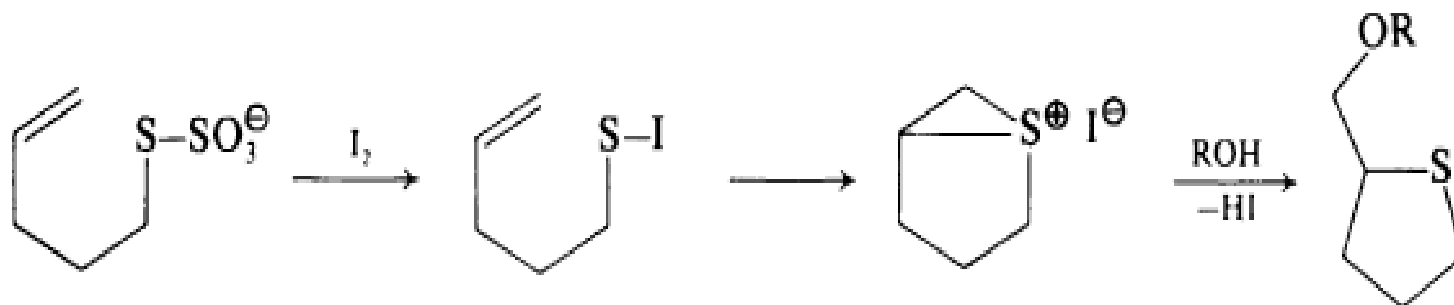


Cyclohexyl metaborate activates alkyl peroxides so that the combination provides effective epoxidizing agents. A good arrangement of soft-hard fragments ready for transfer of an oxygen to olefins is shown. The harder phenyl metaborate reacts with the hydroxy oxygen of tetralin hydroperoxide.

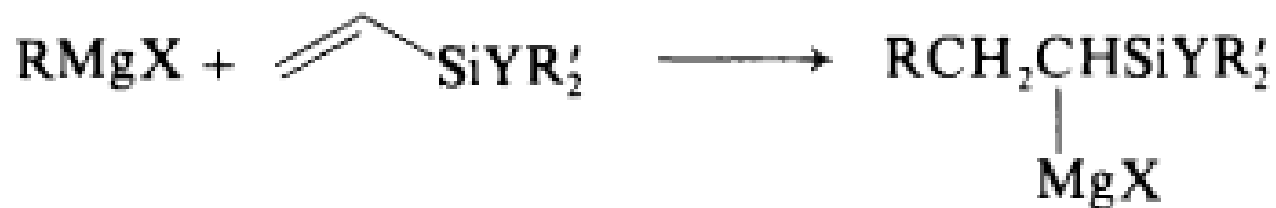


MISCELLANEOUS REACTIONS

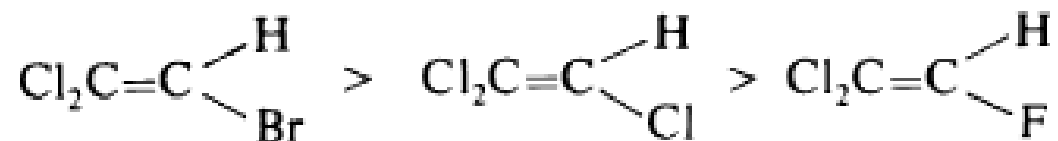
The oxidation of δ,ϵ -unsaturated Bunte salts by iodine leads to tetrahydrothiophenes predominantly; π participation is clearly indicated. The sulfur atom of the sulfenyl iodide intermediates is a very soft acceptor.



The addition of Grignard reagents to vinylsilanes is generally favored by the softer R (tertiary > secondary > primary) in RMgX. Harder reagents such as benzyl-, phenyl-, and allylmagnesium halides effect only displacement at Si, provided that a leaving group is present.



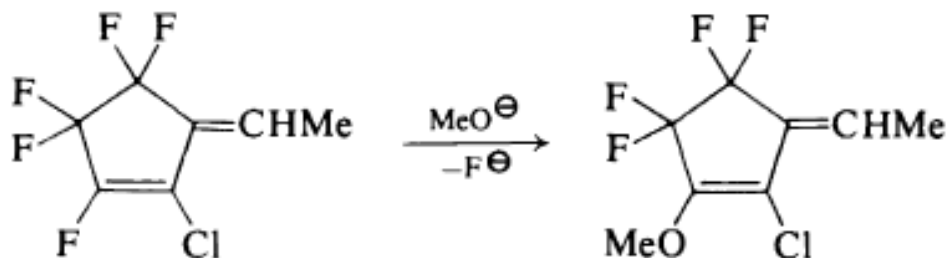
The ease of carbanion formation from halo forms depends on the α halogen as $I > Br > Cl > F$. This same order is valid for haloethylenes as evidenced by the rate of deuterium exchange.



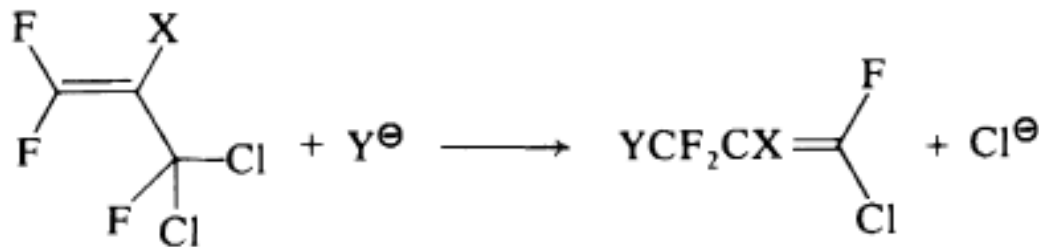
The condensation of sodiostannanes with bromoacetylene gives bromoethynyltin derivatives, instead of the terminal acetylene. Apparently vinyl carbanion intermediates, specifically those stabilized by α -Br, are involved.



The vinylic fluorine is specifically displaced by the hard methoxide ion from a chlorofluorocyclopentene derivative. The existence of transition state symbiosis, as well as the fact that chlorine stabilizes the carbanion better, must be the contributing factors to the specificity.



The S_N2' displacement of fluoropropenes by halide ions Y^- , as shown below, is especially favored by fluoride ion ($F^- > Cl^- > Br^-, I^-$). Symbiosis could be the reason.

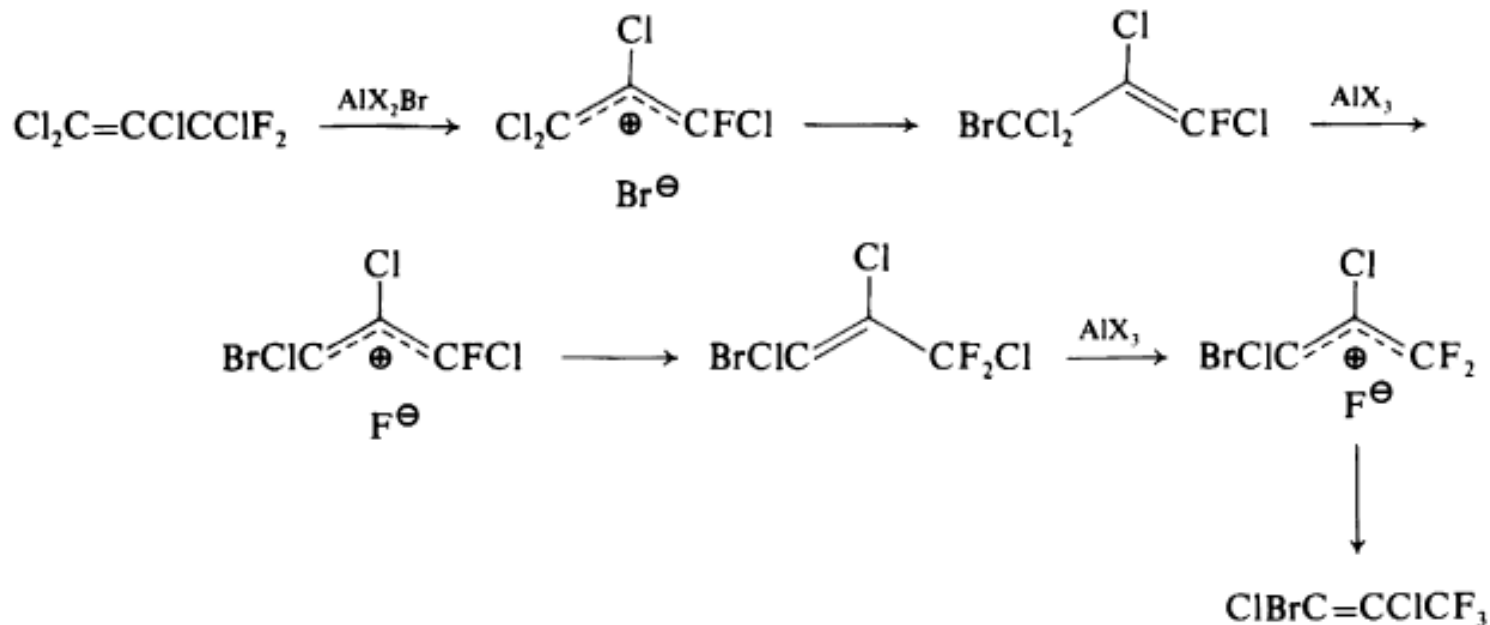


Y = halogen

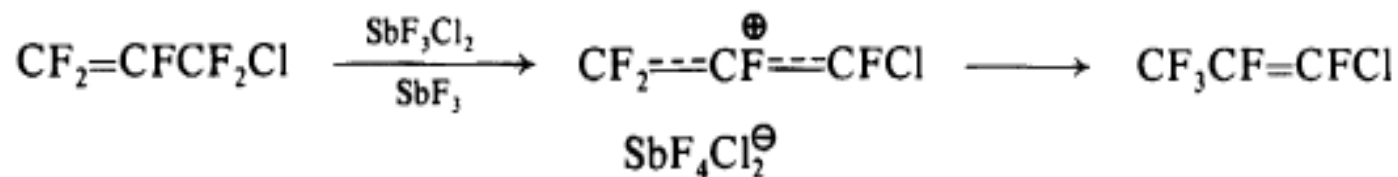
X = H, Cl

Treatment of 3,3-difluorotetrachloropropene with AlBr_3 gives, among other products, 1-bromo-1,2-dichloro-3,3,3-trifluoropropene.

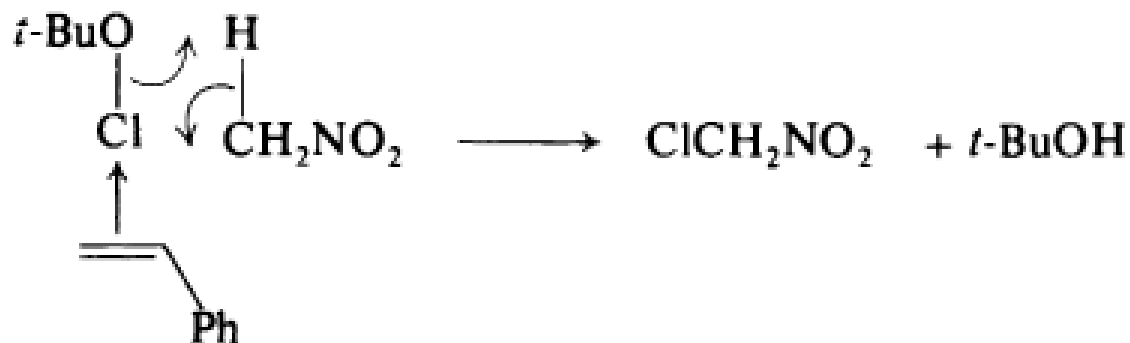
The proposed mechanism invokes successive specific attack of soft (Br^-) and hard (F^-) ions at the softer and harder carbocation centers, respectively. The source of F^- is from other concurrent processes.



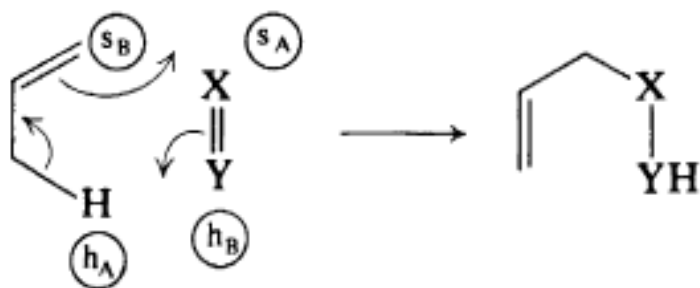
Allylic rearrangement of 3-chloropentafluoropropene goes through an unsymmetrical cation, in contrast to the expectation of ionizing the softer Cl^- . Symbiosis indicates, however, that formation of $\text{SbF}_4\text{Cl}_2^-$ is better than $\text{SbF}_3\text{Cl}_3^-$.



The catalytic effect of olefins on chlorination of nitroalkanes was discovered during an attempt to add *tert*-butyl hypochlorite across the styrene double bond. It appears that a four-centered reaction is facilitated by the soft π complexation as outlined below.



Although the ene reaction is a concerted homopolar process, it is favored by the presence of polar groups in the enophiles. For example, formaldehyde is an active enophile, however, it hardly participates in the Diels-Alder reaction.



Strikingly, hexafluoroacetone undergoes an ene reaction with propene yielding a sulfide instead of a thiol. The thionic sulfur atom acts as a soft acceptor as predicted by the HSAB principle.



The substituent effects on [1,5]sigmatropic ester shift have been scrutinized.

The k_{rel} , increases with the hardness of the substituent R geminal to the migrating ester group.

Perhaps the transition state of the rearrangement resembles the product in which R becomes attached to a harder sp^2 -hybridized carbon atom.

