

University of Tikrit
College of science
Department of Chemistry



A scientific essay :-

Elimination unimolecular conjugated base(E1cB)

&

Elimination bimolecular conjugation(E2c)

Papered by PhD students:-

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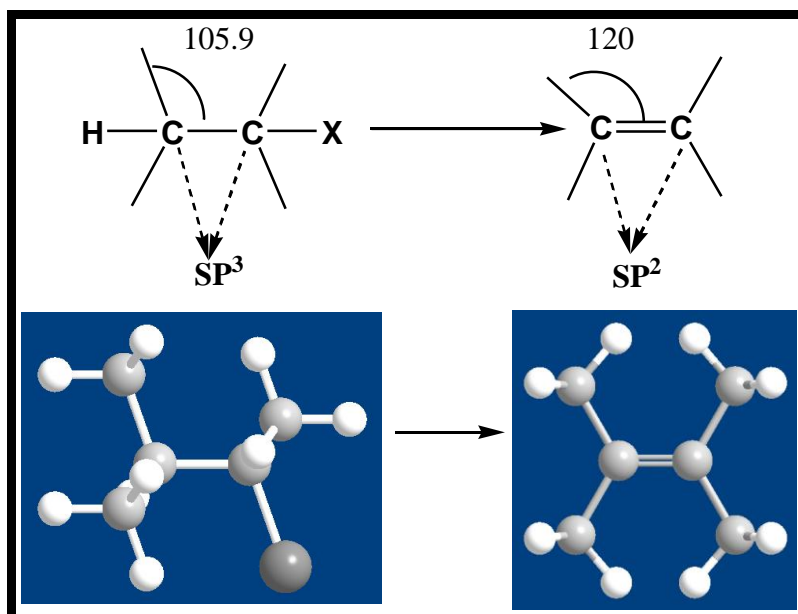
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❖ Introduction

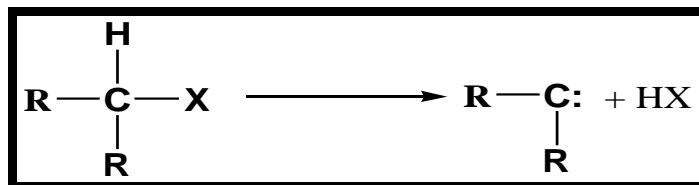
Elimination reactions involve the removal from a molecule of two atoms or groups, without them being replaced by other atoms or groups. In the great majority of such reactions the atoms or groups are lost from adjacent carbon atoms, one of them very often being a proton and the other nucleophile (Y^- or $\text{Y}:$), resulting in the formation of a multiple bond.



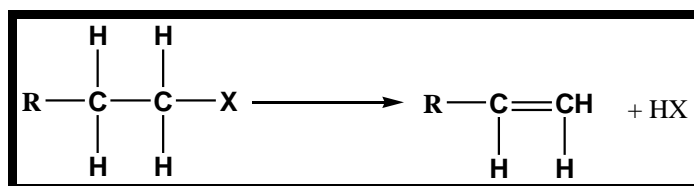
❖ Elimination Reactions of Carbanions

The elimination reactions of carbanions have been put under different classes these are:

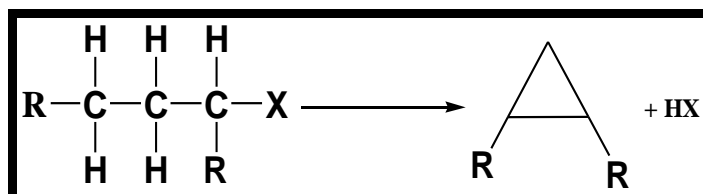
a- α – Elimination



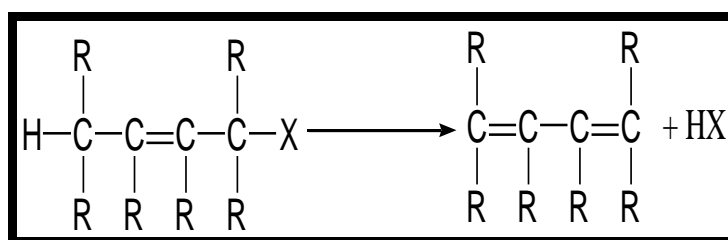
b- β – Elimination



c- γ – Elimination



d- δ ~ Elimination

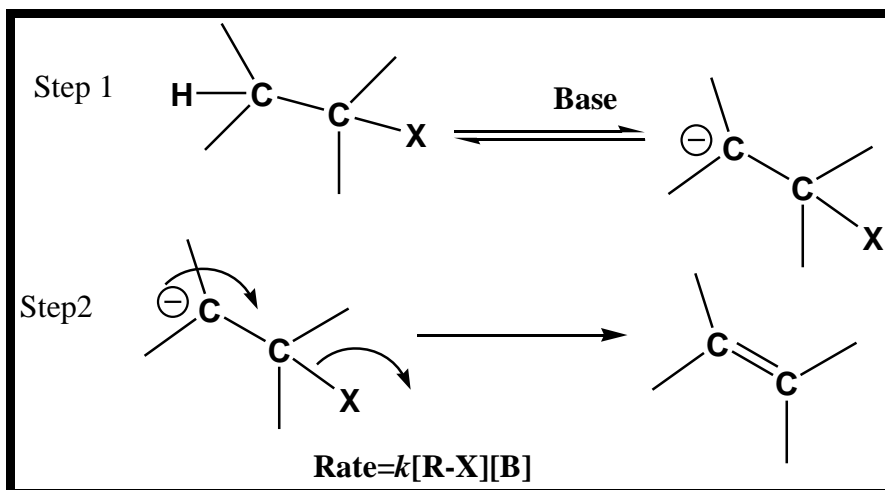


Note

1,4-eliminations have received much less attention Nevertheless, they have important applications in synthetic organic chemistry and play a key role in certain biological processes Mechanistic studies in the condensed phase have shown that syn-1,4-elimination is often but not always the preferred stereochemical course further more base-induced 1,4-elimination can be in competition with 1,2-elimination.

❖ The E1cB Mechanism:

In the E1 mechanism, X leaves first and then H. In the E2 mechanism, the two groups leave at the same time. There is a third possibility, The H leaves first, and then the X. This is a two-step process, called the E1cB mechanism, or the carbanion mechanism, since the intermediate is a carbanion:



The name E1cB comes from the fact that it is the conjugate base of the substrate that is giving up the leaving group. We can distinguish three limiting cases:

1- The carbanion returns to starting material faster than it forms product: step 1 is reversible; step 2 is slow (E1cB)_R.

2- Step 1 is the slow step, and formation of product is faster than return of the carbanion to starting material. In this case, step 1 is essentially irreversible (E1cB)_{irr}.

3- Step 1 is rapid, and the carbanion goes slowly to product (E1)_{anion}.

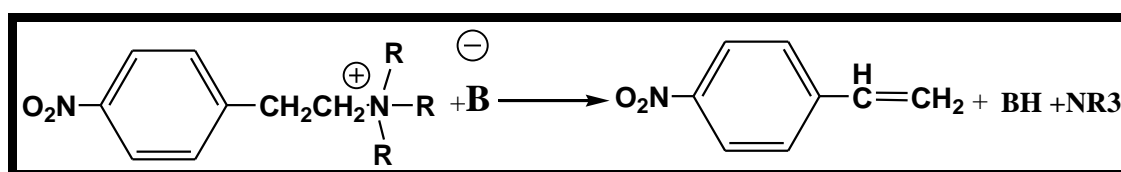
Investigations of the reaction order are generally not very useful (except for case 3, which is first order), because cases 1 and 2 are second order and thus difficult or impossible to distinguish from the E2 mechanism by this procedure. We would expect the greatest likelihood of finding the E1cB mechanism in substrates that have:

- (a) a poor nucleofuge
- (b) an acidic hydrogen, and most investigations have concerned such substrates.

❖ The following is some of the evidence in support of the E1cB mechanism:

1- The first step of the (E1CB)R mechanism involves a reversible exchange of protons between the substrate and the base. In that case, if deuterium is present in the base, recovered starting material should contain deuterium. This was found to be the case in the treatment of $\text{Cl}_2\text{C}=\text{CHCl}$ with NaOD to give $\text{ClC}\equiv\text{CCl}$

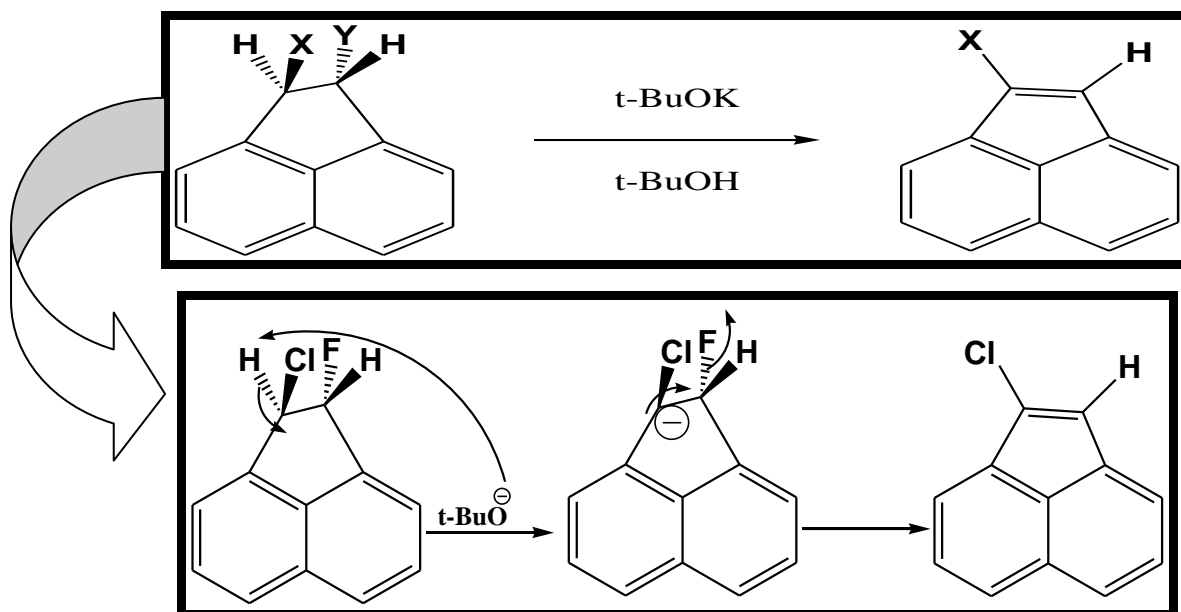
2- When the reaction:



was carried out in water containing acetohydroxamate buffers, a plot of the rate against the buffer concentration was curved and the rate leveled off at high buffer concentrations, indicating a change in rate-determining step.

3- We have predicted that the E1cB mechanism would most likely be found with substrates containing acidic hydrogens and poor leaving groups. Compounds of the type $\text{ZCH}_2\text{CH}_2\text{OPh}$, where Z is an electron-withdrawing group ($-\text{CN}$, $-\text{COOH}$).

Of the three cases of the E1cB mechanism, the one most difficult to distinguish from E2 is (E1cB)I. One way to make this distinction is to study the effect of a change in leaving group. This was done in the case of the three acenaphthylenes

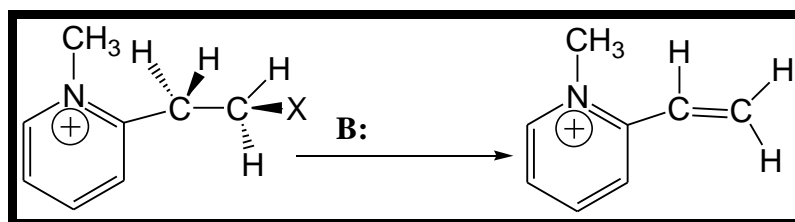


where it was found that:

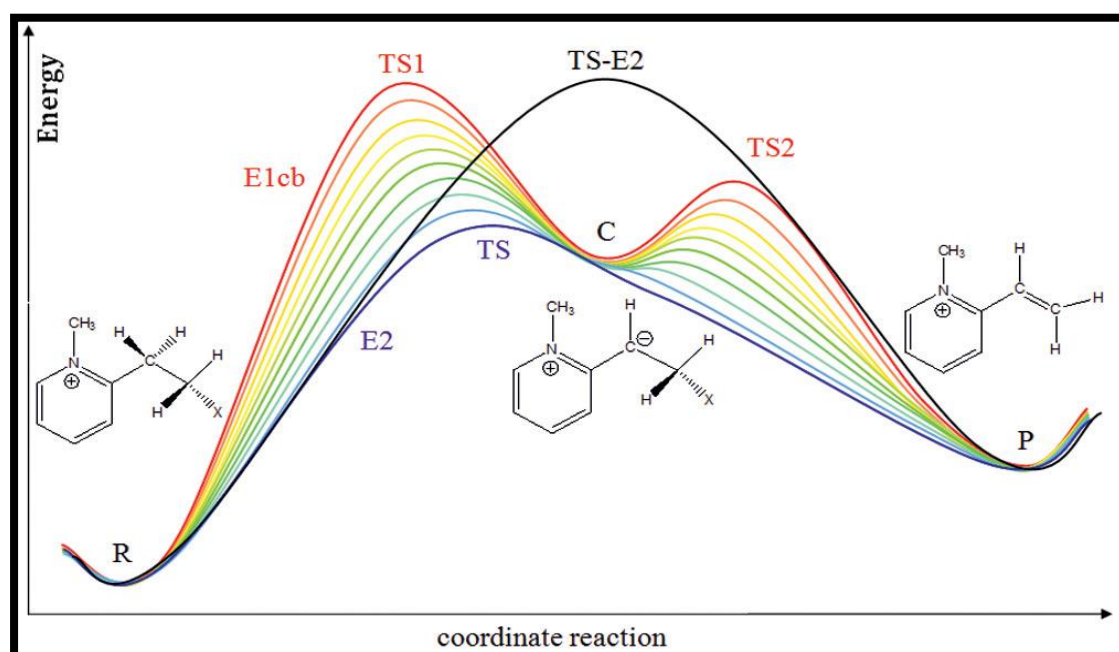
- a- the three rates were fairly similar, the largest being only about four times that of the smallest, (X=Br,Y=Cl).
- b- In compound (X=Cl,Y=F) the only product contained Cl and no F that is only poorer nucleofuge F departed while Cl remained .

❖ Potential energy

The following reaction undergoes through (E1cB) mechanism, and to distinguish



between *E2* and *E1cB* reaction pathways is a daunting task, since the two mechanisms share several common characteristics. On the other hand, which one of the two mechanisms actually prevails may be extremely consequential, in biological systems, where the E1cb carbanion intermediate might undergo undesired collateral reactions. The nature of the borderline region between the two mechanistic regimes has only recently been explored, suggesting, in specific cases, the lack of discontinuity between E1cb and E2 pathways. These results lend support to the classic “merging” theory considered by *More O’Ferrall and Jencks*, in which the two reaction mechanisms merge into each other, leading to a smooth transition between the E1cb and E2 pathways. The possibility of coexistence of the E2 and E1cb mechanisms has also been considered. Potential energy surfaces for merging of (irreversible) E1cb and E2 reaction mechanisms:-





SUMMARY

ElcB

❖ *Stepwise reaction*

❖ *Carbanion intermediate*

❖ *No kind of conclusion*

❖ *Poor leaving groups*

❖ *More acidic B-H*

❖ *Rate = $k[R-X][Base]$*

❖ *Two Steps*

❖ *First Order*

❖ The E₂C Mechanism:

Certain alkyl halides and tosylates undergo E₂ eliminations faster when treated with such weak bases as Cl⁻ in polar aprotic solvents or PhS⁻ than with the usual E₂ strong bases, such as RO⁻ in ROH.⁶⁹ In order to explain these results, Parker⁷¹ proposed a spectrum of E₂ transition states in which the base can interact in the transition state with the α carbon, as well as with the β hydrogen. At one end of this spectrum is a mechanism (called E₂C) in which, in the transition state, the base interacts mainly with the carbon.



The E₂C mechanism is characterized by strong nucleophiles that are weak bases. At the other extreme is the normal E₂ mechanism, here called E₂H to distinguish it from E₂C, characterized by strong bases. Transition state(I & II) represents a transition state between these extremes. Additional evidence for the E₂C mechanism is derived from Brønsted equation considerations:

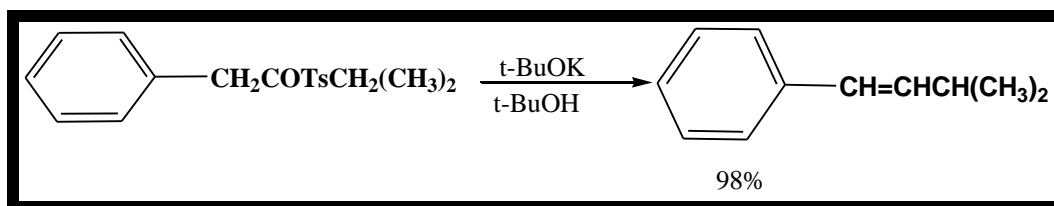
$$\log k = \beta \log K_{\beta} + C, \quad (K = \text{Rate of constant}, \quad k_{\beta} = \text{base of ionization constant})$$

from substrate effects, from isotope effects, and from the effects of solvents on rates. However, the E₂C mechanism has been criticized, and it has been contended that all the experimental results can be explained by the normal E₂ mechanism. Although the actual mechanisms involved may be a matter of controversy, there is no doubt that a class of elimination reactions exists that is characterized by second-order attack by weak bases.

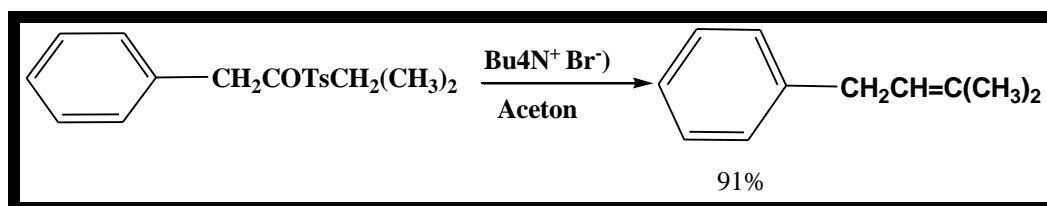
These reactions also have the following general characteristics:

- a- favored by good leaving groups
- b- they are favored by polar aprotic solvents
- c- the reactivity order is tertiary > secondary > primary, the opposite of the normal E_2 order.
- d- the elimination is always anti- (syn-elimination is not found).

As already mentioned, $E2C$ reactions show a strong preference for Zaitsev (*in an elimination reaction the major products formed will be more substituted alkene*) orientation. In some cases, this can be put to preparative use under the usual $E2$ reaction conditions (t-BuOK in t-BuOH). In this case the double bond goes to the side with more hydrogens because on that side it will be able to conjugate with the benzene ring. use for example:



However, with the weak base ($Bu_4N^+ Br^-$) in acetone the Zaitsev product formed:



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- ❖ ***J.Chem.Soc.,Perkin Trans, 1, 2002, 2563-2585.***
- ❖ **Kenneth Wang, A.B. *Candidate in Chemistry/Physics Harvard College* '17 Oct 2014.**