ADVANCED CHEMISTRY BLOC

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INTRAMOLECULAR REACTIONS

Steps move towards lower free energy in the microscopic world of chemical reactions. In this context, entropy has its own contribution. Why a rubber band moves back and forth, though not in a regular rhythm? It has very weak intermolecular forces, rather say very weak forces operating between polymeric fibres in a rubber band. It's an elastomer. In elastomers, entropy is more favoured than enthalpy. It likes to remain in its original random conformation favoured by entropy. Similarly, intramolecular reactions are favoured by entropy. A single molecule reacts to produce two or higher number of fragments thereby contributing towards the feasibility of the process.

Intramolecular reactions may involve oxidation-reduction. On heating some substances, a powerful oxidising agent within the substance gets enough activation energy to reduce some other component of the same substance.

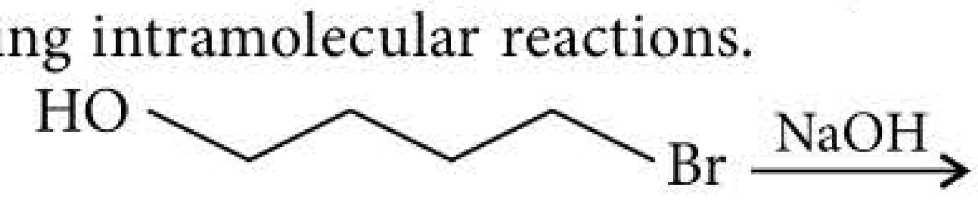
$$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$$

'Pb' due to inert pair effect is maintaining its +2 state but it is the 'N' which is an oxidising agent. Though, this reaction can be classified as thermal decomposition but we can also classify it as intramolecular redox reaction. You fix a 'basis' to classify the things. When you change the basis, things emerge in a different way. That is why you have so many ways of classifying the things.

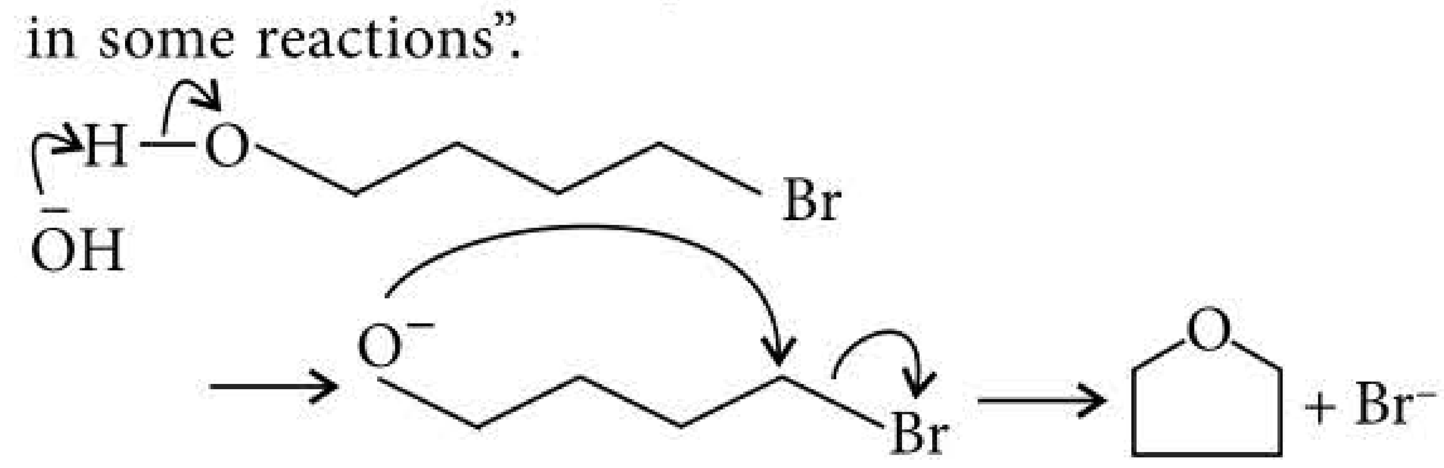
Another similar example is

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + H_2O$$

In a similar way, a number of other thermal decompositions may be included. Keeping them aside, we can move to organic chemistry to see some interesting intramolecular reactions.



Generally, you never say alcohol is enough acidic to react with NaOH. But when you say you actually mean, the acid-base reaction between alcohol and NaOH is not a product favoured equilibrium. Few molecules of alcohol may loose proton which may pave the path of reaction. It's surely worth noting "Less frequent molecular collisions may decide the fate of molecule in some reactions".

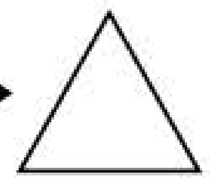


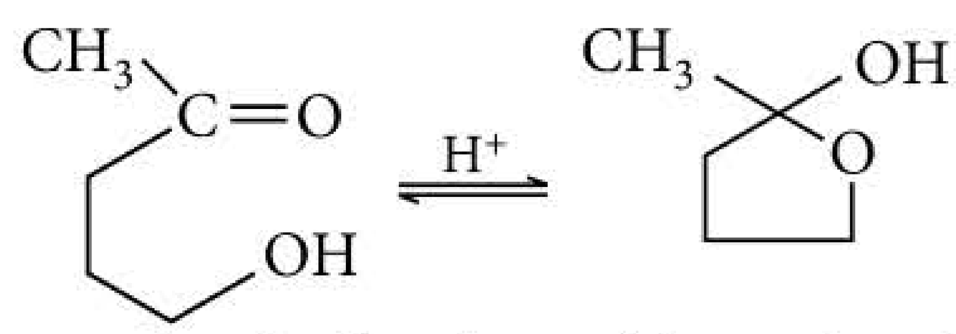
Look at the loss and gain. The random conformations of the open chain reactant is now lost. A ring cannot have so many conformations as open chain compound. Again, two fragments are formed, an ether and a Br^- ions. There is gain in entropy, which is strong enough to overpower the loss in entropy due to loss in conformations. But what if the upcoming ring is a six-membered one? Naturally, you have a longer open chain compound as starting material and you are likely to loose more random conformations during cyclisation. This may not be an encouraging situation and this is indeed true. "Rate constant for ring closing reaction is higher for five membered ring than six membered ring".

Another important parameter is "probability of ring closing". It's easy to fold a smaller chain into a ring than a longer chain. Probability of ring closing is therefore highest for three membered ring formation. But as you know, a three membered ring is under heavy strain. Therefore, ring closing reactions roughly proceed at the rate :

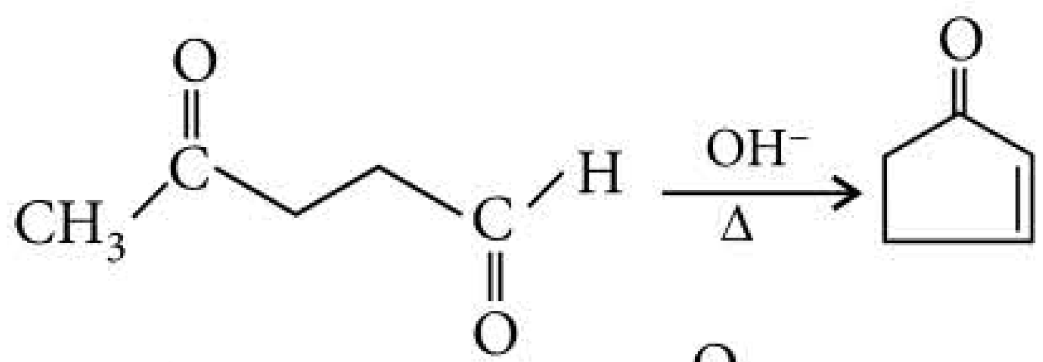
$5 > 6; \quad 3 > 4$

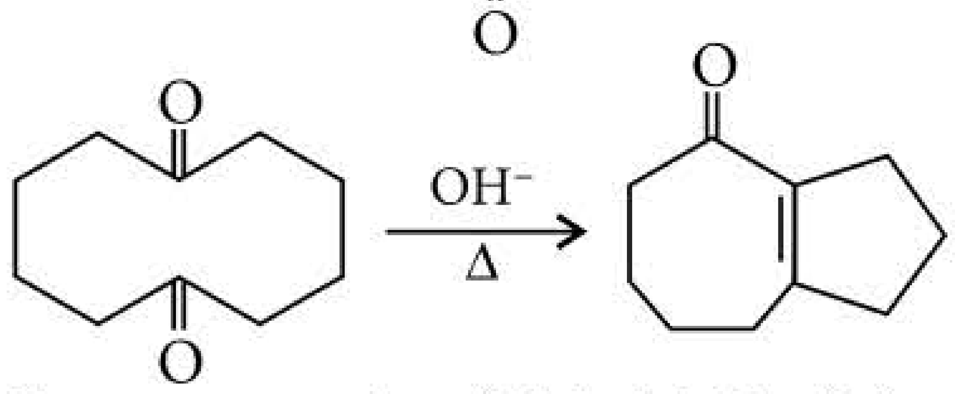
Loss of entropy due to cyclisation, probability of ring closing and ring strain together decide this trend and moreover intramolecular ring closing is favoured over intermolecular reactions.

$$Br-CH_2-CH_2-CH_2-Br \xrightarrow[\text{ether}]{Mg}$$ 

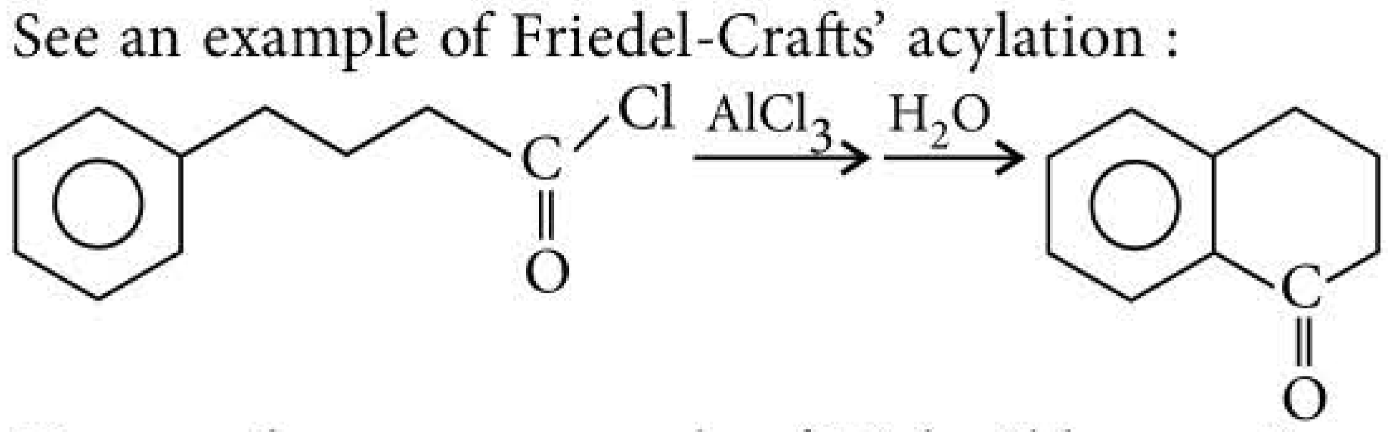


It's an intramolecular hemiacetal formation. Similarly, intramolecular aldol condensations are very common.

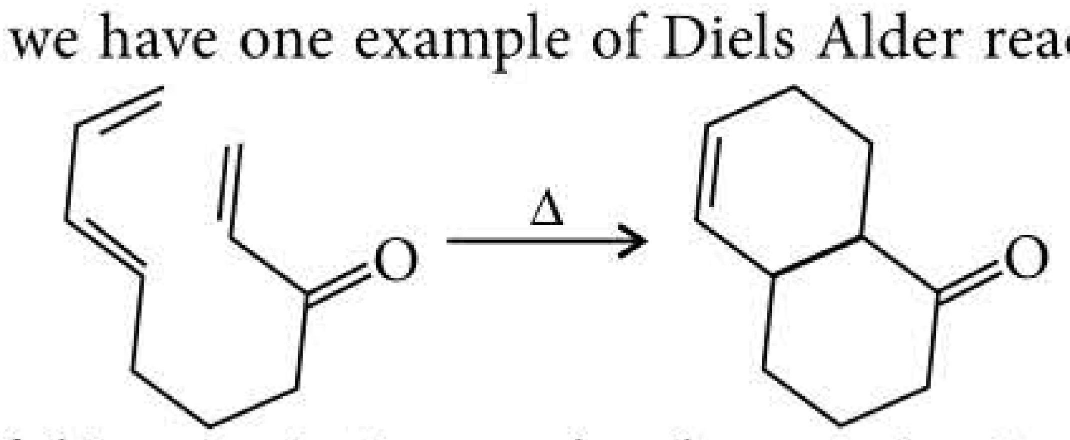




See an example of Friedel-Crafts' acylation :



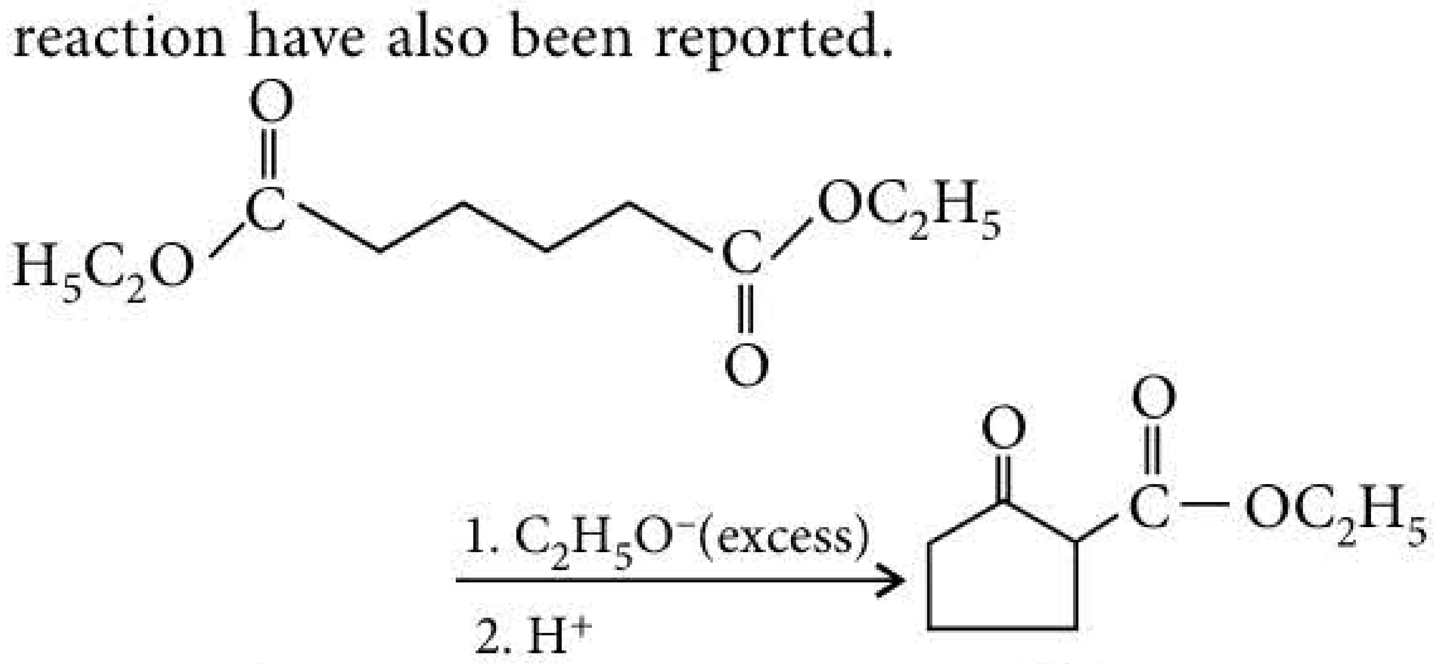
Here, we have one example of Diels Alder reaction :

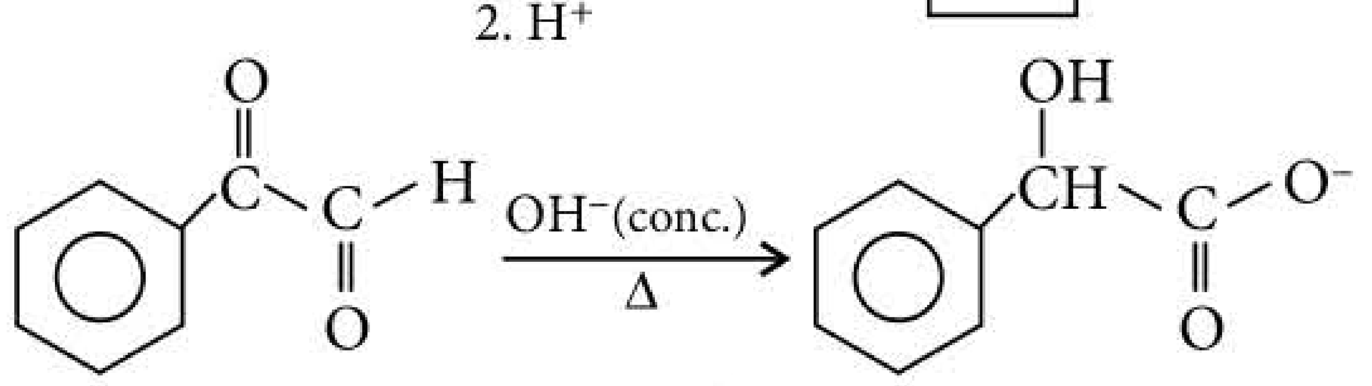


A useful inorganic intramolecular reaction is :

$$\underset{\text{Adduct}}{BH_3.NH_3} \xrightarrow{200\,°C} B_3N_3H_6 + H_2$$

Intramolecular Claisen condensation, Cannizzaro reaction have also been reported.





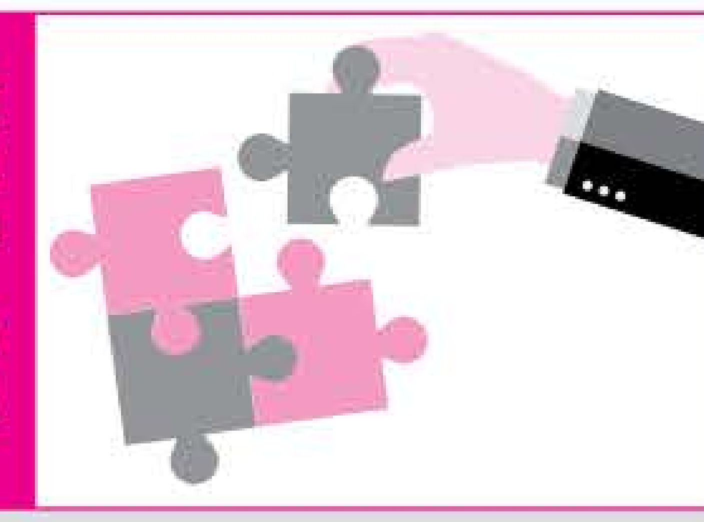
Few important reactions of inorganic compounds are :

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + HCl + H_2O$$

$$ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} ZnO + HCl + H_2O$$

H_2O present in the compound hydrolyses the chloride to form hydroxide, which subsequently decomposes to give oxide.

PUZZLE CORNER



CHEMDOKU

In this puzzle 6 × 6 grid is given, your objective is to fill the digits 1-6 so that each appear exactly once in each row and each column.

Notice that most boxes are part of a cluster. In the upper-left corner of each multibox cluster is a value that is addition, subtraction or multiple (as indicated) of its numbers. For example, if that value is 3× for a two-box cluster, you know that only 1 and 3 can go in there. But it is your job to determine which number goes where! A few cluster may have just one box and that is the number that fills that box.

Note : Atomic masses of the given elements to be considered as your answer.

Clues :

a+			b×		
c+		d×			e+
f−	g×			h×	
			i+		
	j+				

(a) In gaseous form it is used as a blanketing gas and in liquid form it is used as a refrigerant to freeze foods, soft or rubbery materials.

(b) It is a silvery white lustrous metal, which is obtained by electrolysis of its chloride or fluoride. It is used for removing sulphur from petroleum and also to remove traces of water from alcohol.

(c) A very important element, which when mixed in liquid form with finely divided carbon, acts like dynamite in coal mining.

(d) It is a toxic silvery metal which occurs as mineral monazite and used to produce special dark glasses.

(e) This noble gas remains unadsorbed on charcoal even at −180 °C when mixture of noble gases brought in contact.

(f) It was first liquefied by James Dewar in 1898 by using regenerative cooling and vacuum flask and next year he produced its solid form.

(g) One of its isotope has half life 5.7×10^3 years and constantly being produced by reaction between cosmic ray neutrons and nitrogen in upper atmosphere.

(h) It is a silvery-yellow metal, used in permanent magnets and in conjunction with other compounds it is used to kill cancer cells.

(i) It is non-metallic, extremely hard (very strong crystalline lattice) coloured solid. Its pure form is obtained from reduction or pyrolysis of its halides.

(j) Its batteries are used wherever a reliable current is required for a lengthy period. Pacemaker battery is an example of this type of batteries.

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