

Combustion. *Burning of alkanes in the presence of oxygen* is known as **combustion**. Complete combustion results in the formation of carbon dioxide and water, and a large amount of heat is evolved. This is the basis of the fuel value of natural gas, gasoline, kerosene and diesel oil. Combustion is the main reaction occurring in an internal combustion engine where a compressed mixture of alkanes and air is made to burn. Although combustion is an extremely exothermic reaction, it requires a very high temperature (of a flame) to initiate the reaction. This initial high temperature in the engine is supplied by the 'spark ignition'. Once started, the reaction produces sufficient heat to continue combustion.

The compression ratio is very important for the working of an engine. A higher compression ratio makes the gasoline engine more efficient, but it results in **knocking**. Knocking is a phenomenon where instead of all the fuel burning smoothly, some of it burns with an '*explosive violence*' due to a premature ignition of the fuel. It greatly reduces the efficiency of the engine and increases its wear. Different fuels have different knocking tendency which is expressed by a number known as **octane number**. *The higher the octane number, the lower the knocking tendency.*

Experiments with pure compounds have shown that different hydrocarbons differ widely in their knocking tendency which is probably related to their structures because, in general, the straight-chain alkanes tend to produce much more knocking than the branched-chain alkanes, and the anti-knock tendency increases with the extent of branching. 2,2,4-Trimethylpentane (also improperly known as '*isooctane*' in industry) has been found to burn, in internal combustion engine, much more smoothly (without knocking) than any other hydrocarbon, and was arbitrarily assigned an octane number of 100. On the other hand, *n*-heptane produces much more knocking than any commercial fuel, and was assigned an octane number of zero. An *octane number scale* has been set up for rating a fuel or another hydrocarbon, with isooctane at one end of the scale and *n*-heptane at the other, and the octane numbers ranging between 100 and zero corresponding to the volume percentage of isooctane in the isooctane-heptane mixtures. Thus, the octane number of a fuel is the percentage of isooctane in an isooctane-heptane mixture that has the knocking property similar to that of the fuel being tested. For example, a gasoline that has the same knocking characteristics as a mixture composed of 80% isooctane and 20% *n*-heptane, would be rated as 80-octane gasoline.

The octane rating of a fuel may be increased either by adding a small amount of tetraethyllead, $(C_2H_5)_4Pb$, which is known as an '*anti-knock*' agent, or by a process known as *reforming* which is accomplished by subjecting the fuel to catalytic cracking.

Preparation of Alkanes

Generally, organic compounds are obtained in two ways: (i) isolation from natural sources and (ii) preparation from other compounds. In nature, organic compounds occur in varying amounts, and usually along with other compounds. Some compounds occur in nature so abundantly that they are available on commercial scale. The methods of their isolation depend on the nature of the compounds to be isolated, the nature of other compounds present and the purpose for which the compounds are required. In certain

cases, the compounds present in a mixture resemble so closely in their properties that the separation of any one compound in pure form is not possible, neither it is always necessary because for many purposes the mixture may be just as suitable as a pure compound. This has already been manifested by the various fractions of petroleum.

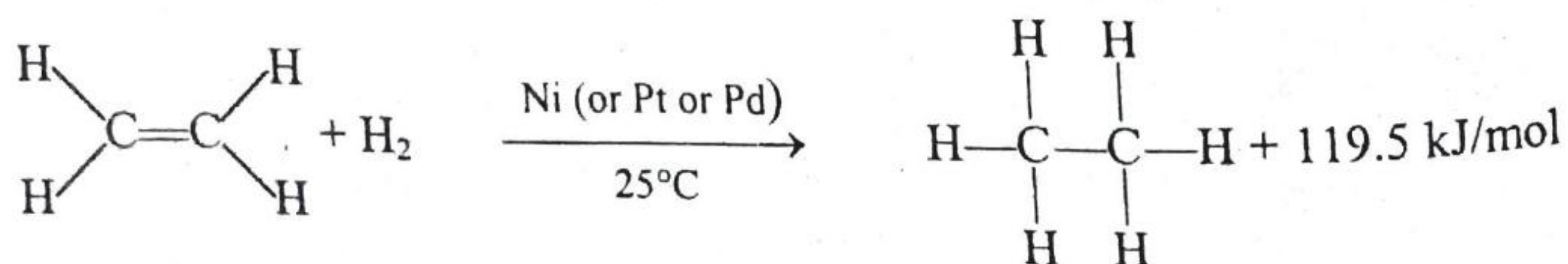
The preparation of organic compounds is usually undertaken on two different levels: (i) industrial level and (ii) laboratory level. On industrial level, the primary consideration is the large scale production at a low cost, purity of the compound may not be very important. However, it may be desirable to separate it from a mixture of products particularly when the other components are also commercially useful. An industrial method for the preparation of a particular compound may not be suitable for the preparation of other members of its family.

In the laboratory, a compound may be required to be prepared in very small quantities, even in nanograms (10^{-9} g); the cost is usually not important. However, it is always desirable to get the compound in pure form and in a very good yield. A laboratory method should be of a general nature and should be applicable to most of the members of a particular family. It may be of interest to develop a laboratory method for the preparation of a compound that is also abundantly available in nature because the same method may be, when the need arises, used for the preparation of a more complex molecule with a similar functional group. For example, ethane, although sufficiently available from the petroleum industry, was synthesised by the hydrogenation of ethylene. Later, the same method was used for the conversion of cholesterol into cholestanol.

Thus, it is not surprising if an industrial method of preparing an organic compound is quite different from a laboratory method of its preparation. In this text we shall concentrate on the more versatile laboratory methods, rather than on the industrial methods of limited applications, for the preparation of organic compounds.

So, some of the general methods used for the preparation of alkanes are given below. The reaction equations are usually written in a generalized form, using the symbol R that represents any alkyl group, to show that the reaction is applicable more or less to the entire family. The symbol X is used for the halogen family.

1. Hydrogenation of alkenes. Addition of hydrogen to a multiple bond is called **hydrogenation**. Alkanes can be prepared by the catalytic hydrogenation of alkenes. When a solution of an alkene in ethanol, methanol or acetic acid, is shaken under a slight pressure of hydrogen gas, in the presence of a small quantity of finely divided nickel, platinum or palladium, at room temperature, the alkene is readily converted to the corresponding alkane in excellent yield (see p. 134).



Although the reaction is highly exothermic, it will not take place even at an elevated temperature without the use of a catalyst because the energy of activation of this reaction is very high (equal to the bond dissociation energy of the hydrogen molecule which is 435 kJ/mol). The energy of activation is greatly lowered by the use of a catalyst.

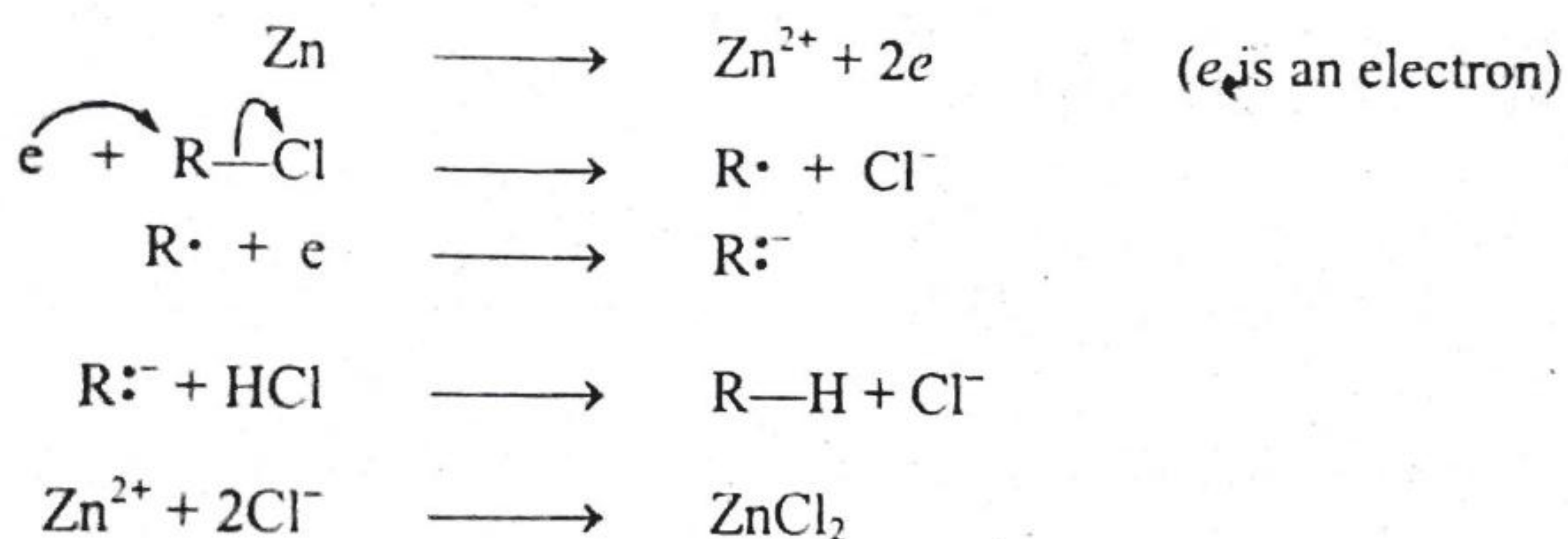
It is a general method for the conversion of a carbon-carbon double bond into a carbon-carbon single bond, and can also be used on industrial scale. Production of vegetable ghee by the catalytic hydrogenation of vegetable oil is one example of the application of this method on industrial scale.

2. Reduction of alkyl halides. Alkanes can be prepared by the reduction of alkyl halides, which may be brought about in different ways.

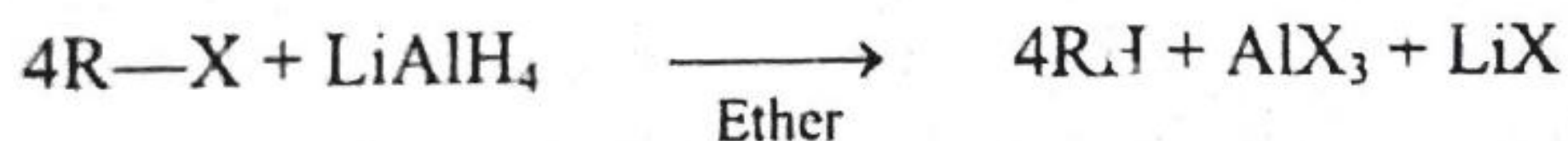
(i) *Reduction by dissolving metals.* An alkane is produced when an alkyl halide is made to react with zinc in the presence of an aqueous acid, such as hydrochloric acid or acetic acid.



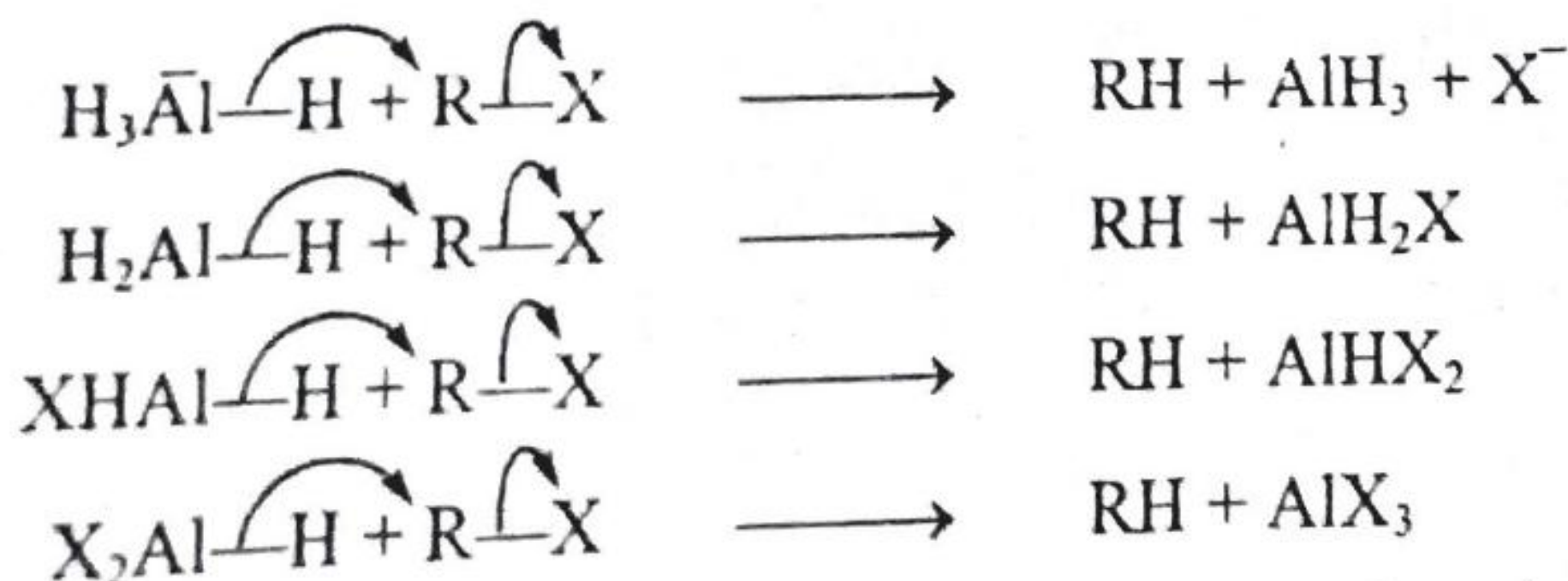
The reaction involves the transfer of electrons from the metal to the substrate, followed by the transfer of proton from the acid, as shown below:



(ii) *Reduction by lithium aluminium hydride.* Lithium aluminium hydride (LiAlH_4) readily reduces primary and secondary alkyl halides to alkanes (tertiary alkyl halides mainly give alkenes).

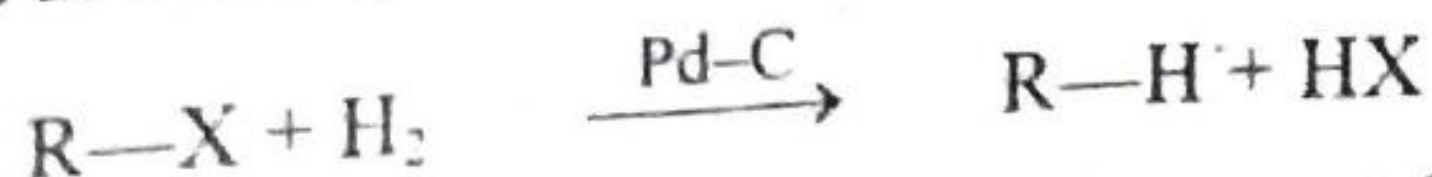


The hydride transfer occurs as follows:



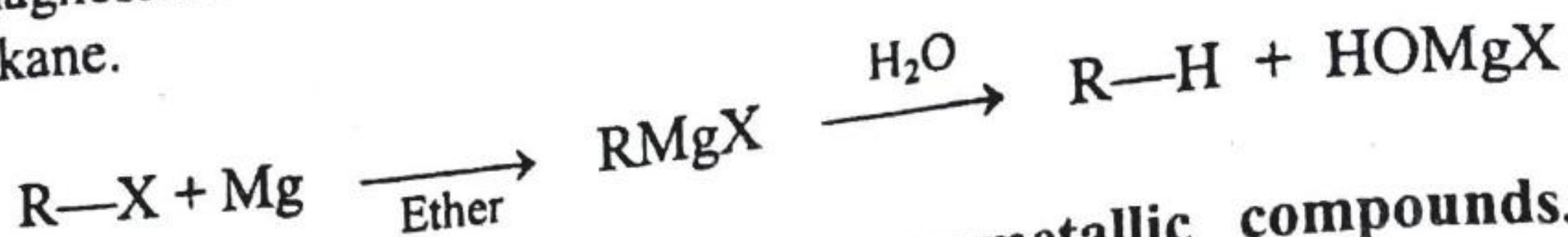
Tertiary (and also secondary) alkyl halides are reduced by sodium borohydride (NaBH_4) which does not reduce primary alkyl halides. On the other hand, triphenyltin hydride (Ph_3SnH) reduces all the three types of halides.

(iii) *Catalytic hydrogenolysis.* Alkanes can also be prepared by the **hydrogenolysis** (hydrogenation accompanied by bond cleavage) of alkyl halides in the presence of palladium-charcoal, used as a catalyst.

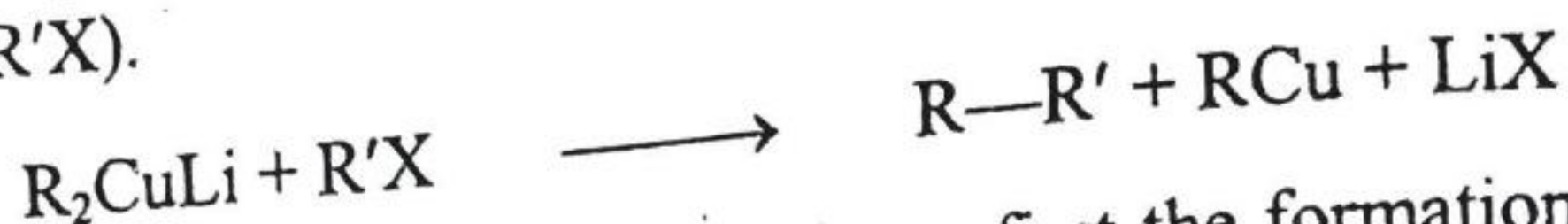


3. Hydrolysis of Grignard reagents. A Grignard reagent (alkylmagnesium halide, RMgX) which is formed when a solution of an alkyl halide in dry ether is allowed to

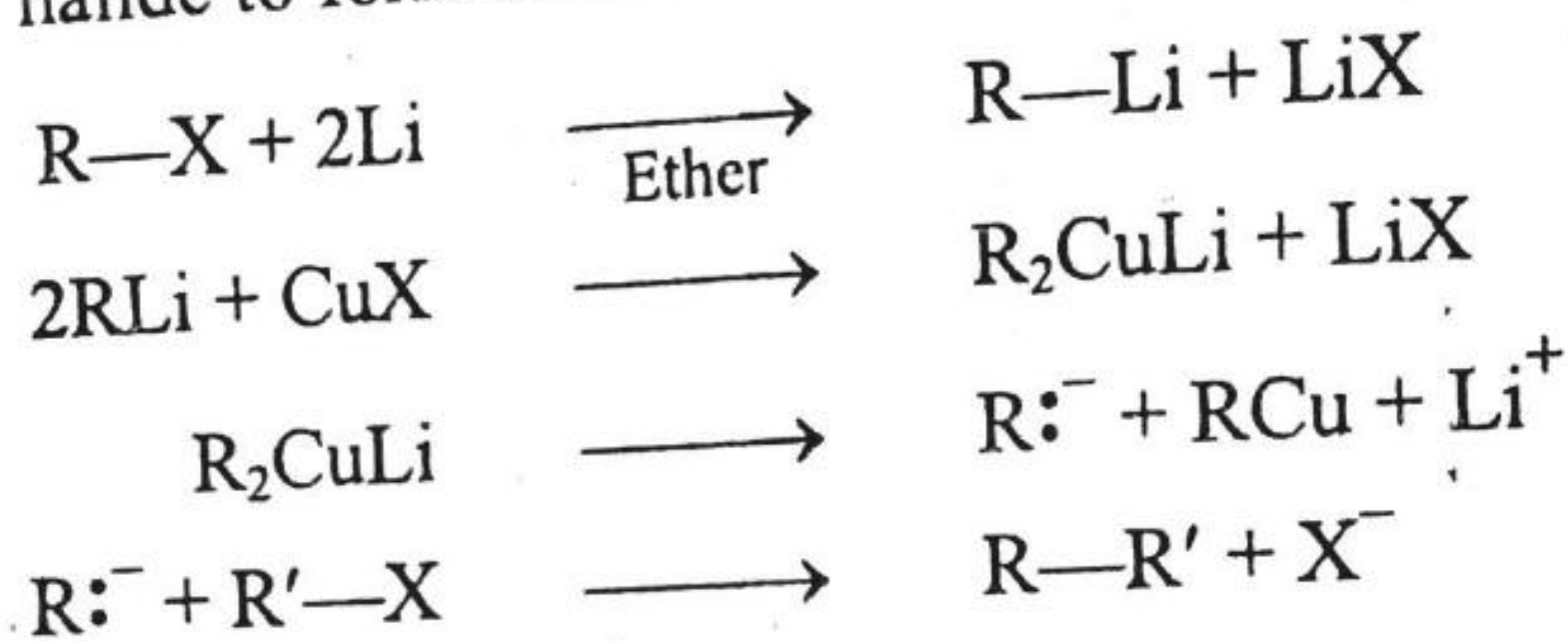
stand over magnesium turning, is a highly reactive species and reacts readily with water to form an alkane.



4. **Coupling of alkyl halides with organometallic compounds.** An alkane containing higher number of carbon atoms than the starting material is formed by the coupling of two alkyl groups when a lithium dialkylcopper (R_2CuLi) is made to react with an alkyl halide ($\text{R}'\text{X}$).

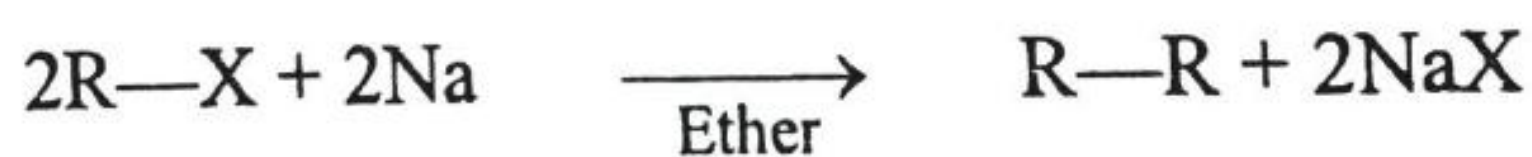


This is known as **Corey-House method** and involves first the formation of alkyllithium (RLi) from an alkyl halide in much the same way as a Grignard reagent. Cuprous halide is then added to alkyllithium to produce lithium dialkylcopper which is then made to react with another alkyl halide to form an alkane.

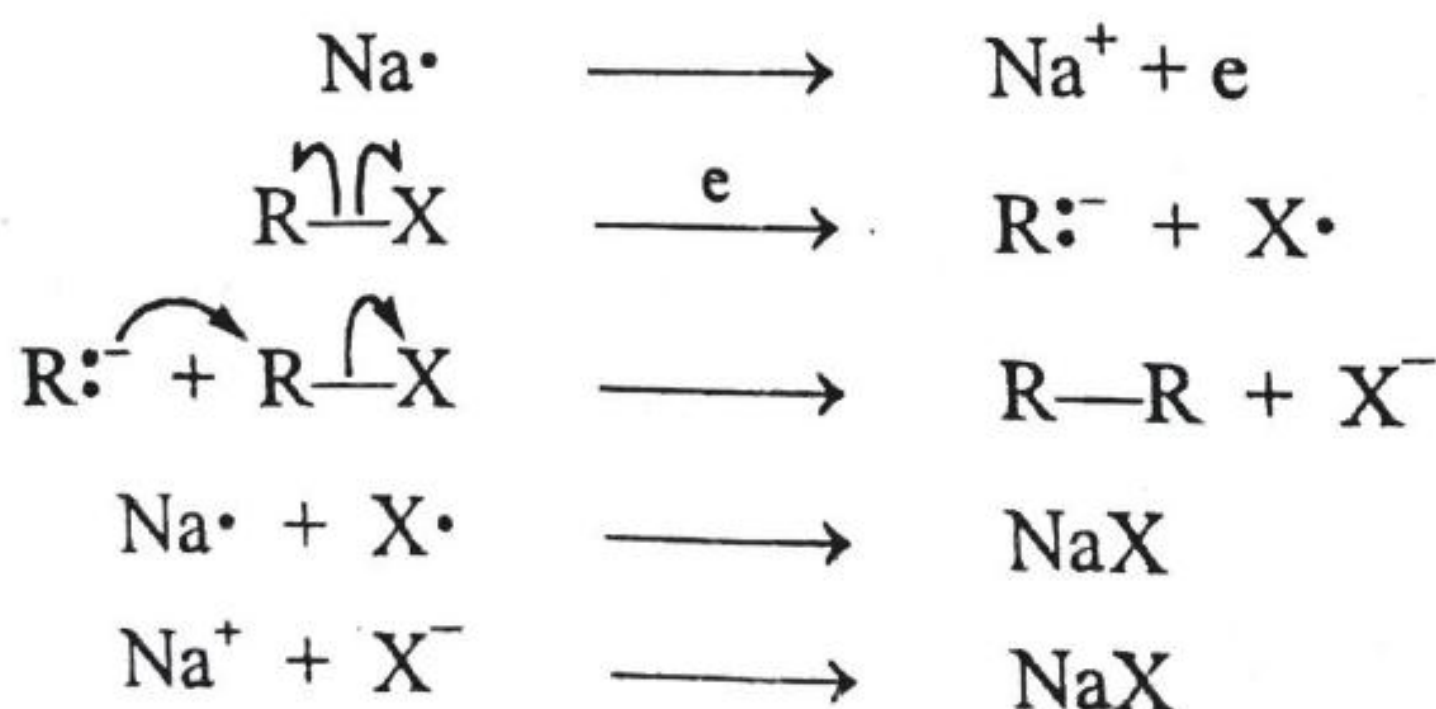


A better yield is obtained if R' is a primary alkyl group; the alkyl group, R , of the organometallic species may be primary, secondary or tertiary.

5. **Wurtz reaction.** Symmetrical alkanes with even number of carbon atoms (R-R) may be formed in a very good yield when an ethereal solution of an alkyl halide (preferably bromide or iodide) is treated with sodium metal.

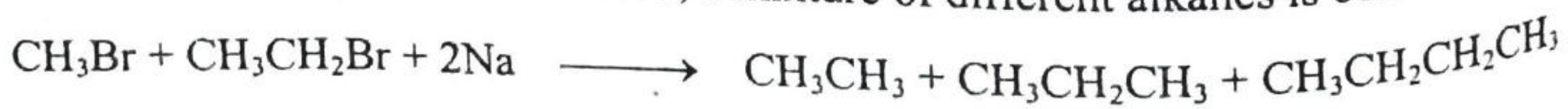


The most probable mechanism involves the intermediate formation of an organosodium compound followed by a bimolecular nucleophilic substitution.



This reaction is not suitable for tertiary alkyl halides due to a side reaction involving elimination.

If two different alkyl halides are used, a mixture of different alkanes is obtained.

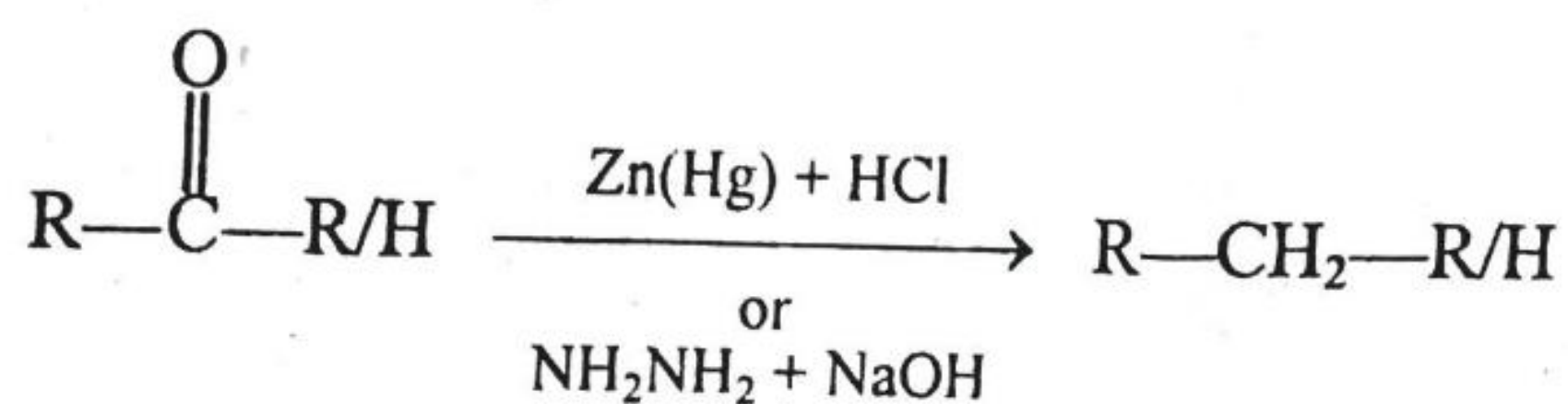


6. Coupling of alkylboranes. A very useful method for the preparation of long-chain alkanes involves the coupling of alkylboranes by means of silver nitrate in the presence of sodium hydroxide at room temperature.



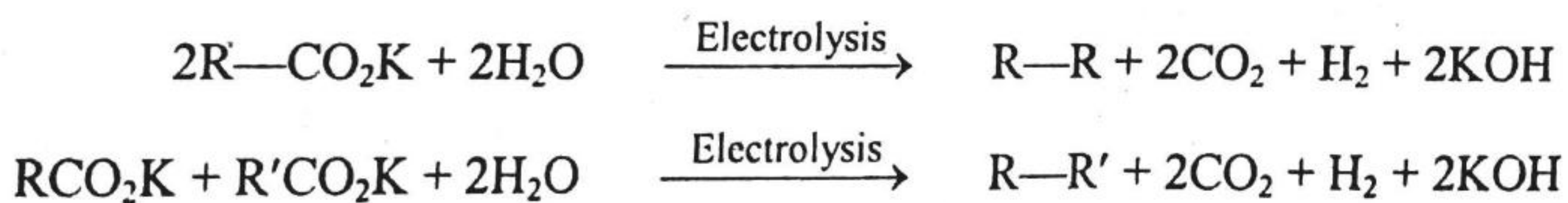
Coupling may also be affected between different alkylboranes.

7. Reduction of carbonyl compounds. Alkanes may also be prepared by the reduction of an aldehyde or a ketone either by amalgamated zinc and hydrochloric acid (*Clemmensen reduction*) or by hydrazine and a strong base such as sodium hydroxide or sodium ethoxide (*Wolff-Kishner reduction*); the carbonyl group is converted to methylene group. The reaction is carried out at an elevated temperature (200°C).

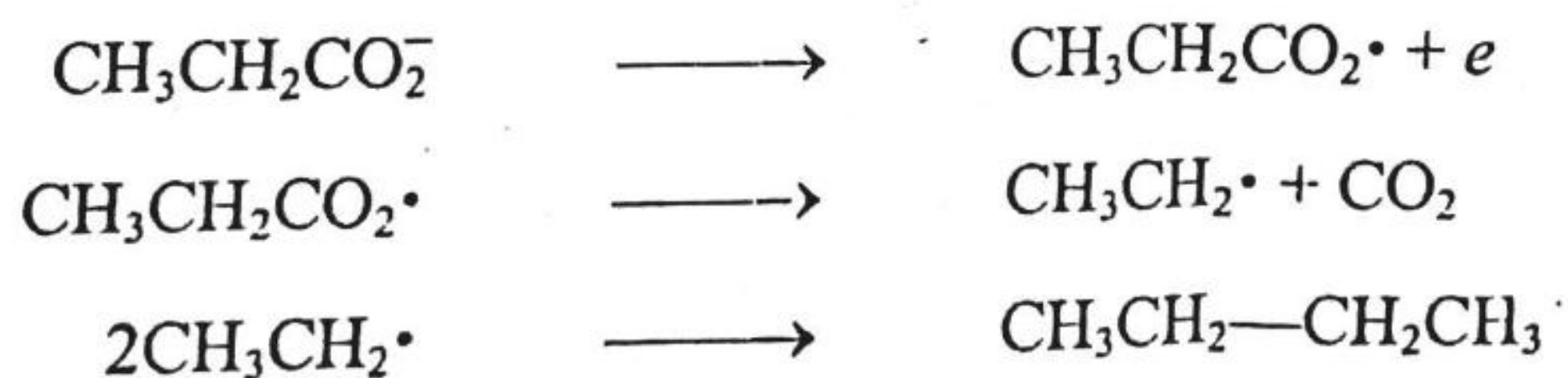


This method is particularly useful for ketones.

8. Kolbe reaction. Electrolysis of a concentrated solution of sodium or potassium salt of a carboxylic acid, or a mixture of two carboxylic acids, yields an alkane with higher number of carbon atoms.



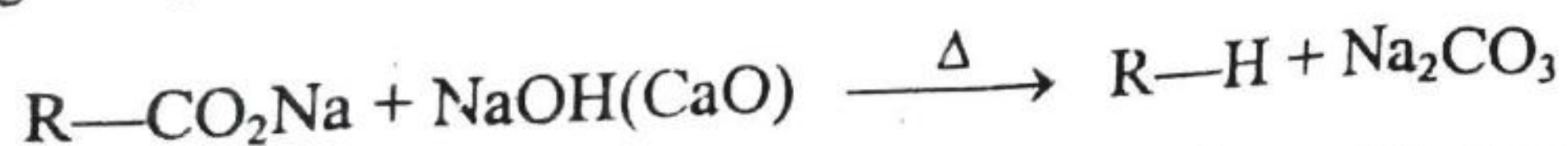
The reaction is considered to involve a free-radical mechanism.



Ethane, ethylene and ethyl propionate are the other products formed in this reaction.

This method has also been successfully applied to the synthesis of natural products, particularly the lipids.

9. Decarboxylation. When a mixture of sodium salt of a carboxylic acid and soda lime is heated together, an alkane is formed with the elimination of carbon dioxide.



This method is only suitable for acetate because in other cases a mixture of various products is obtained whose separation is usually difficult. It is therefore not a useful general method for the preparation of alkanes.