

Chemistry

B.Sc. Sixth Sem.

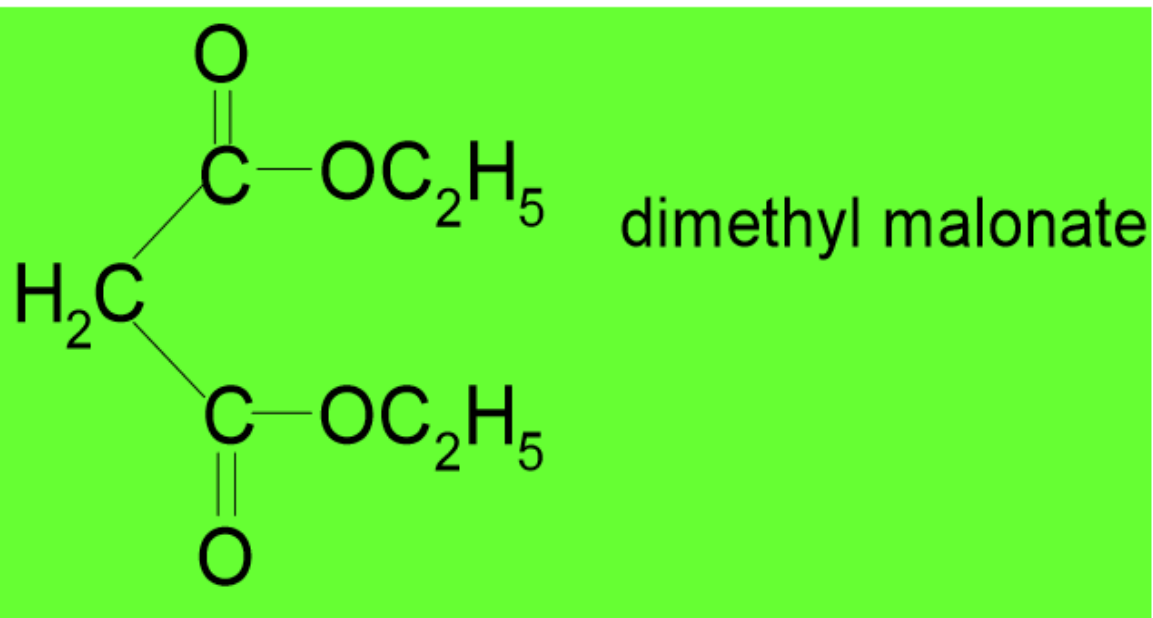
ORGANIC SYNTHESIS VIA

ENOLATES

LECTURE - 2

By Prof. Ranjana Sharma

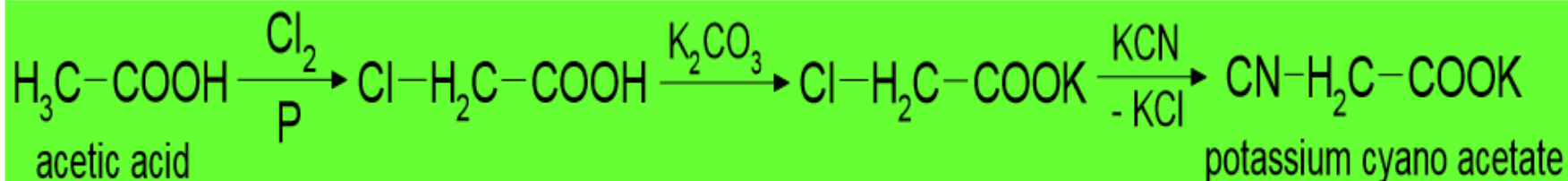
Diethyl Malonate (Malonic ester)



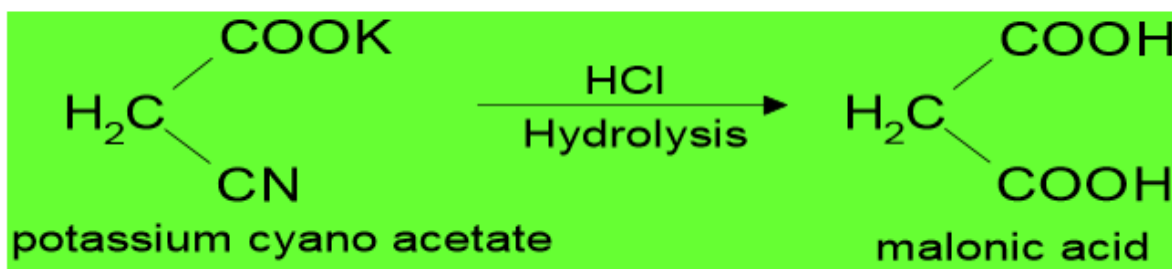
Preparation of diethyl Malonate: -Potassium cyano acetate

on acidic hydrolysis gives malonic acid which on further esterification with ethyl alcohol gives diethyl malonate. It occurs in following steps.

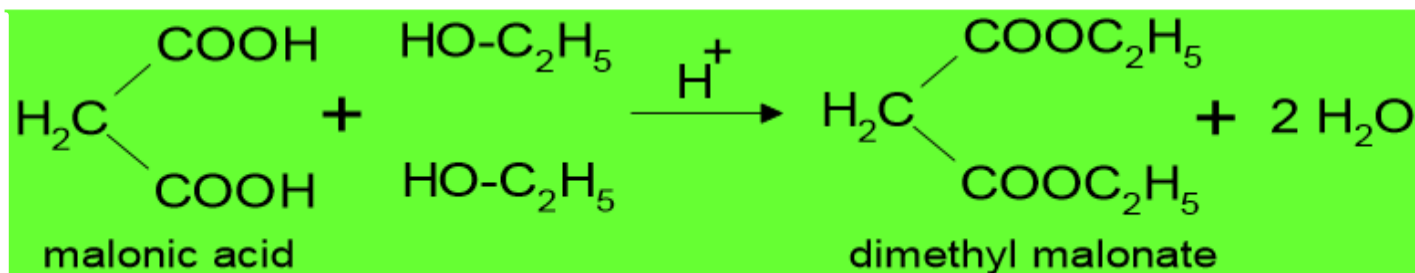
i. Potassium cyano acetate is prepared from acetic acid.



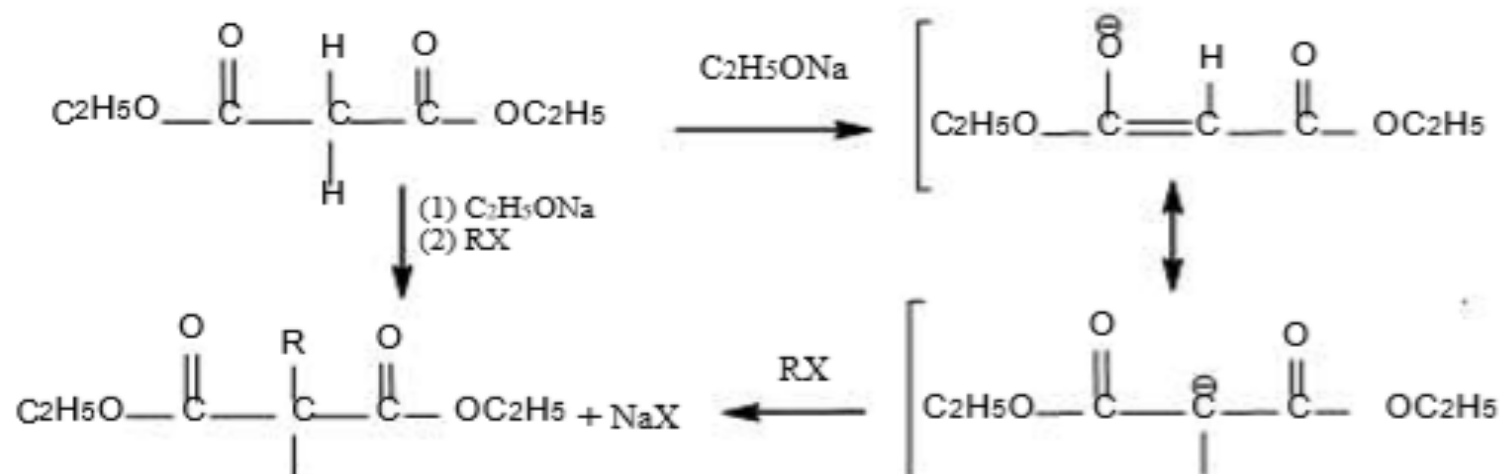
ii. Potassium cyano acetate on hydrolysis with HCl gives malonic acid.



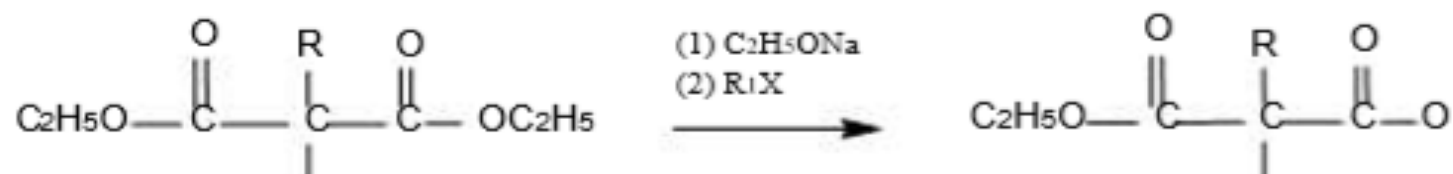
iii. Malonic acid on esterification with ethyl alcohol gives diethyl malonate.



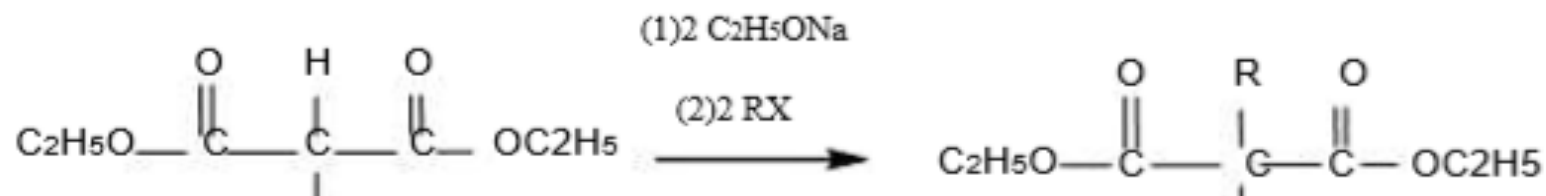
2. **Alkylation of diethylmalonate:** With **sodium ethoxide**, it forms a sodium derivative called as sodiomalonic ester. This reacts with compounds containing a reactive halogen atom, e.g., alkyl halides, acid chlorides, halogen-substituted esters, etc.



The process on repetition produces the disubstituted derivative of malonic ester.

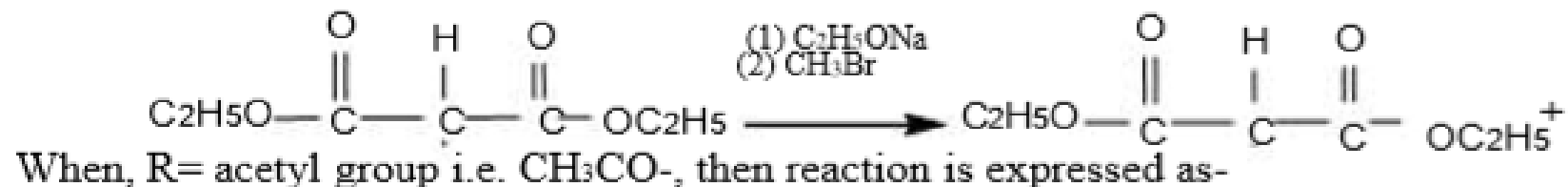


These substituted derivatives of malonic ester can also be readily prepared in *one* step by treating the ester with *two* equivalents of sodium ethoxide and then with *two* equivalents of alkyl halide. This procedure is used only if two identical alkyl groups are to be introduced.



As mentioned earlier, R may be alkyl, acetyl, acyl or halogen substituted ester.

When, R= methyl group i.e. -CH₃, then reaction is expressed as-

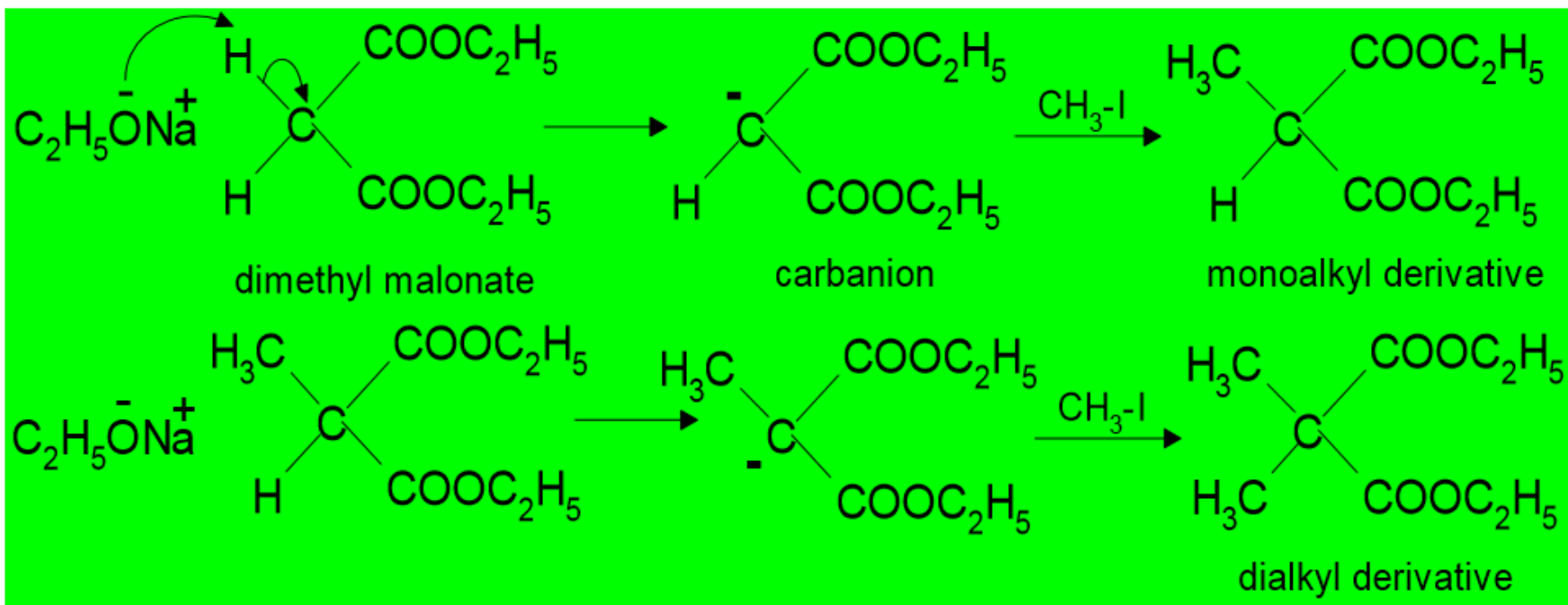


Tertiary Alkyl Halides are not used for Alkylation because they undergo Elimination rather than Substitution to form Alkene.

Synthetic Applications of Malonic Ester

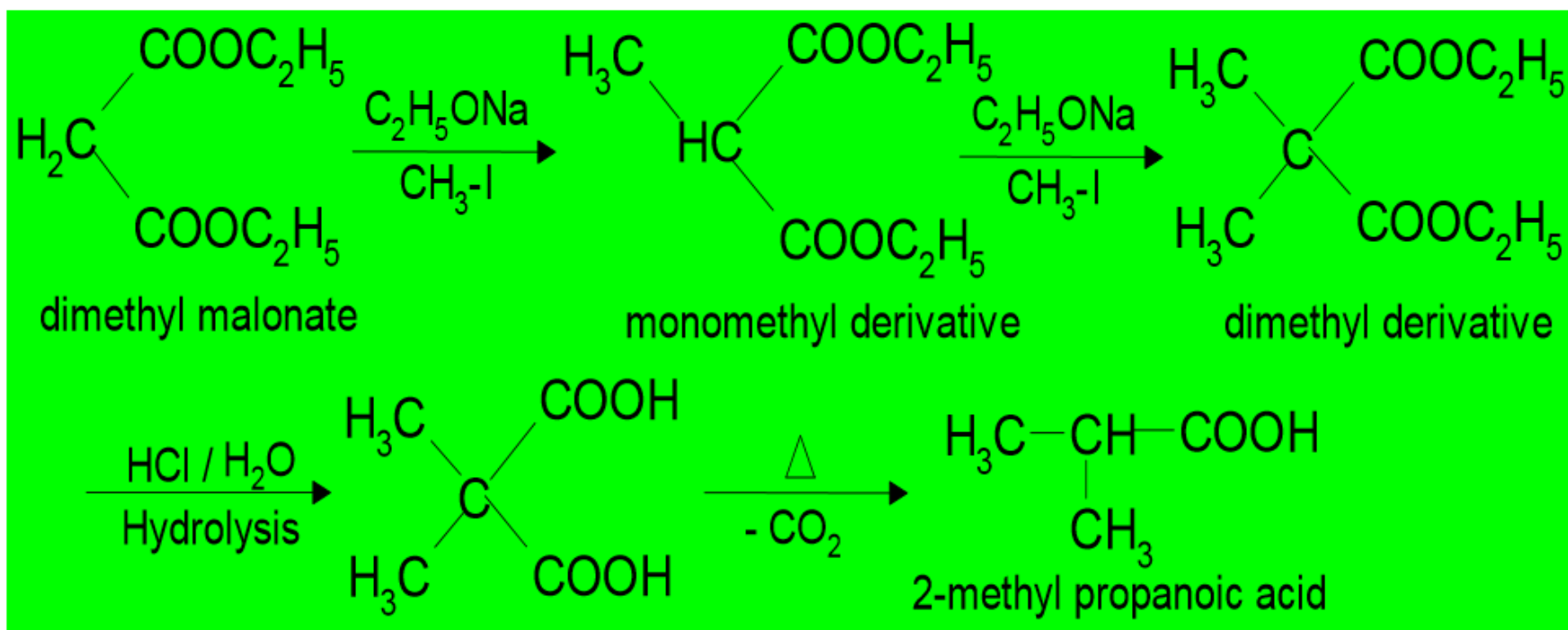
1. Synthesis of alkyl Derivative: -

- Diethyl malonate on treatment with sodium ethoxide gives carbanion which when treated with alkyl halide gives **mono alkyl derivative**. This mono alkyl derivative further on treatment with sodium ethoxide followed by reaction with alkyl halide gives **dialkyl derivative**.



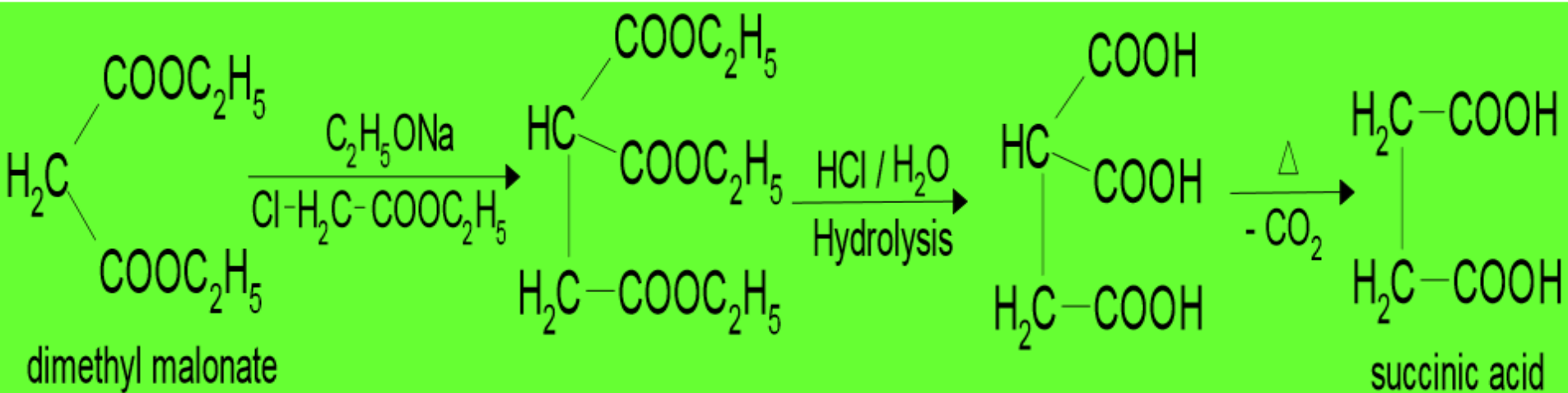
2. Synthesis of Mono-carboxylic acid: -

- Malonic ester on alkylation gives dimethyl derivative of malonic ester which on acid hydrolysis followed by decarboxylation gives **2-methyl propanoic acid**.

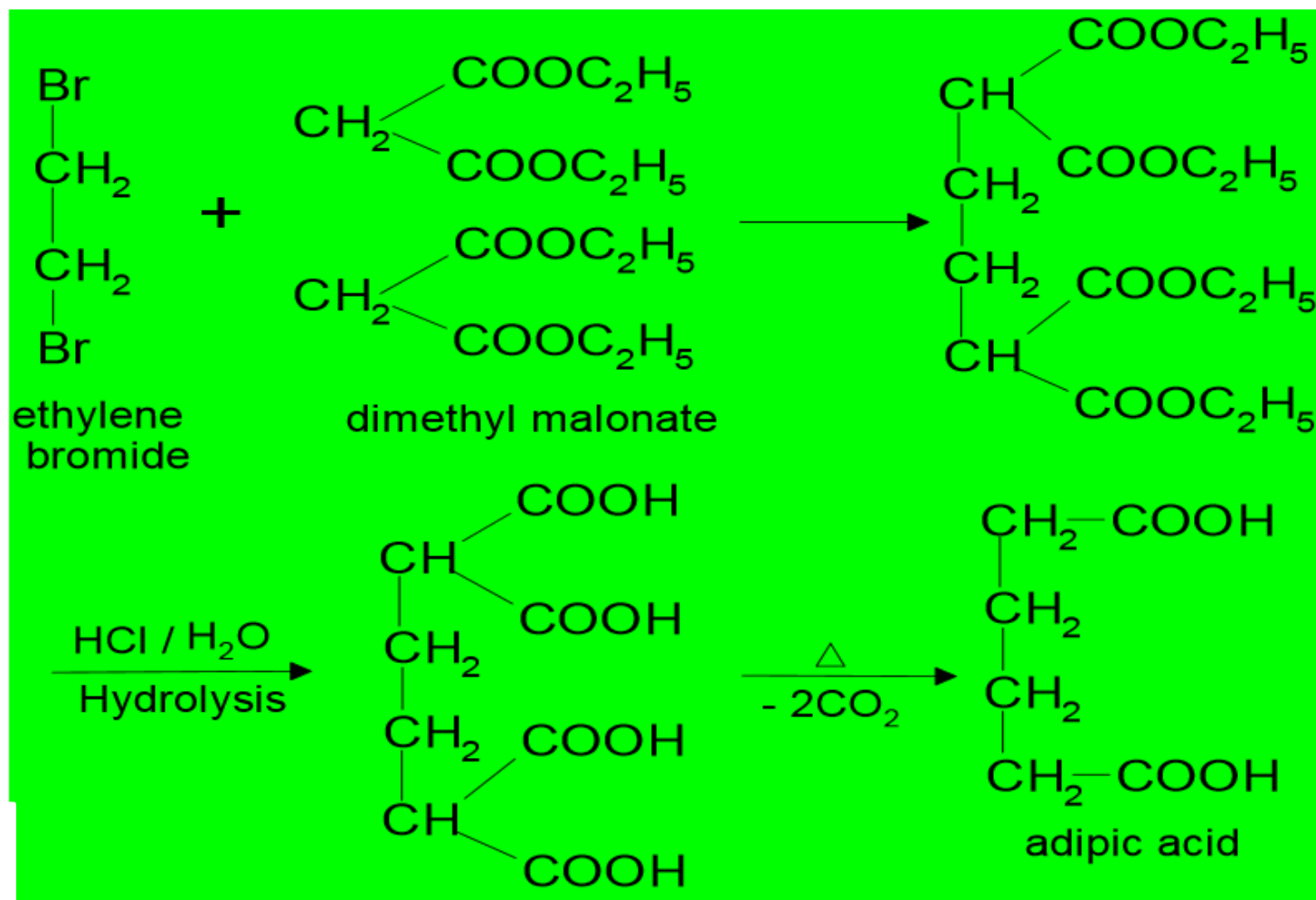


3. Synthesis of Dicarboxylic acid: -

- Malonic ester on treatment with sodium ethoxide & ethyl chloro- acetate gives intermediate which on hydrolysis followed by decarboxylation gives **succinic acid**.

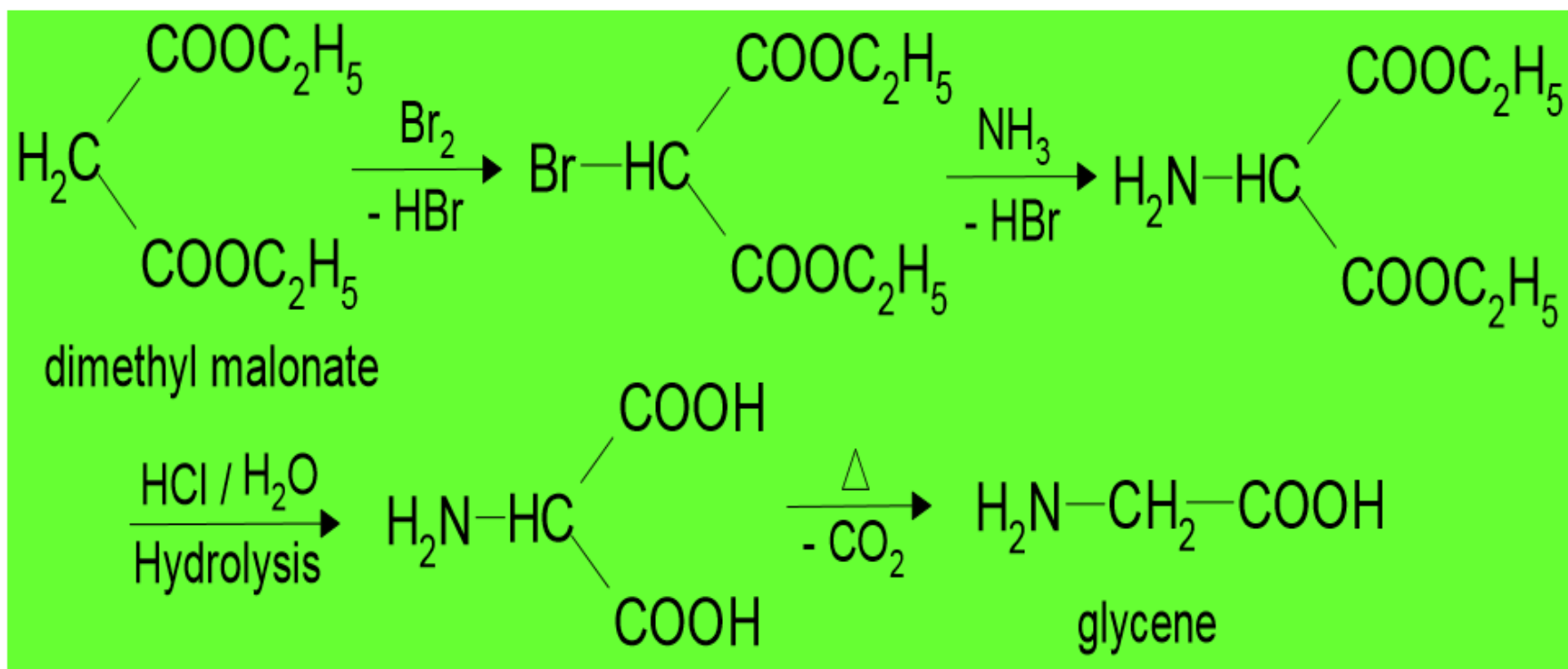


- Diethyl malonate on treatment with sodium ethoxide and ethylene dibromide gives intermediate. This intermediate on hydrolysis & followed by decarboxylation gives **adipic acid**.



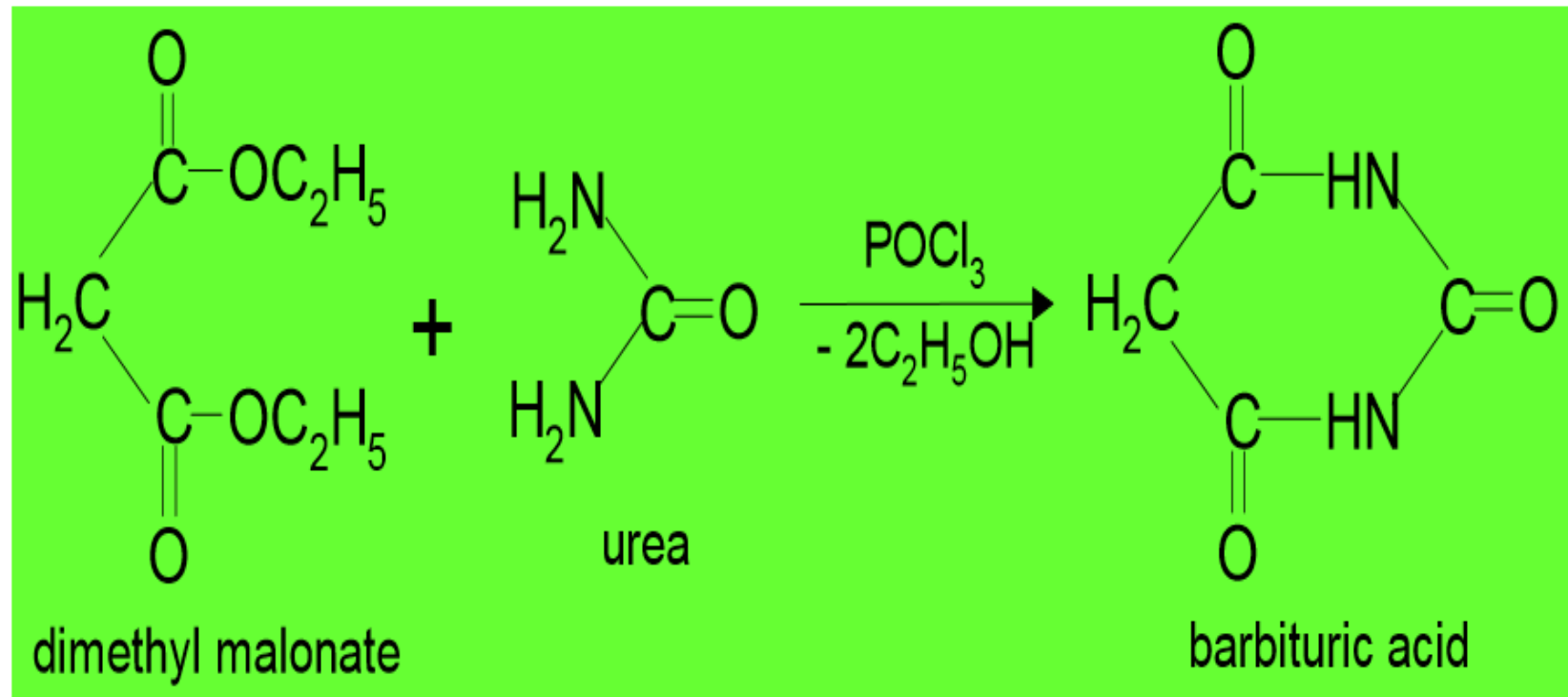
5. Synthesis of glycine (amino acetic acid): -

- Diethyl malonate on treatment with bromine gives diethyl bromo malonate which on treatment with ammonia gives diethyl amino malonate on hydrolysis followed by decarboxylation gives glycine.



6. Synthesis of Barbituric acid:-

- Malonic ester on condensation with urea gives barbituric acid.



End

of

Lecture - 2