ORGANIC NAMED REACTION

DEGREE-III (H) , PAPER-VII

DIEL'S ALDER REACTION CONTINUED...

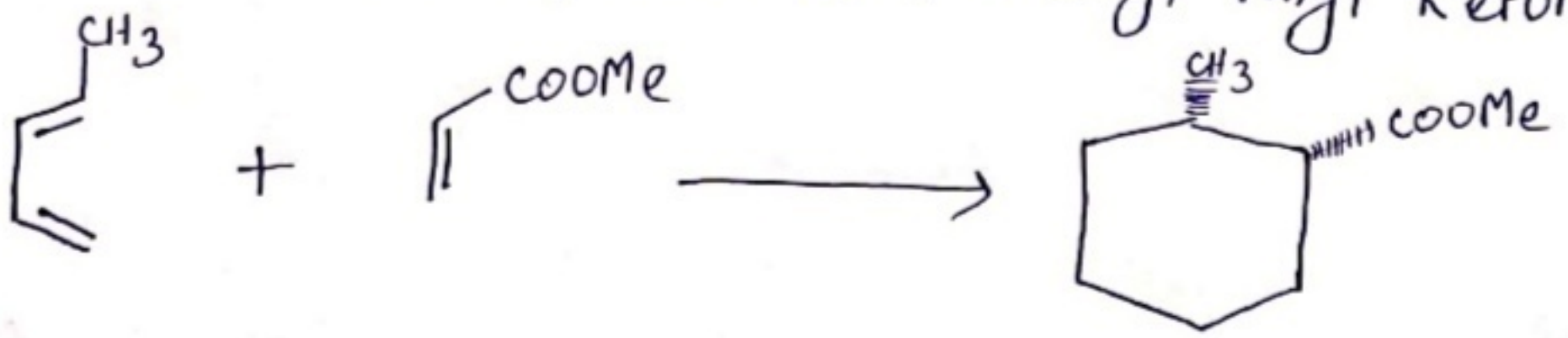
LECTURE-7,DATE :19/09/2020

REGIOCHEMISTRY

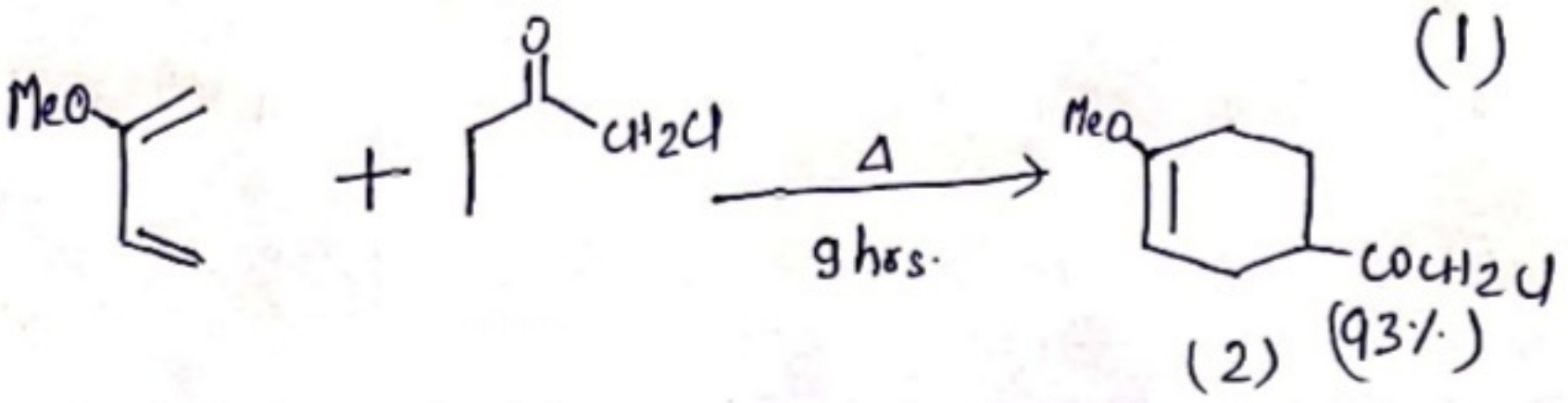
* 1-substituted dienes usually give a mixture in which 1,2-product (1) predominates.

Similarly, 2-substituted dienes give a mixture in which 1,4-product (2) predominates.

* The yield of para product can be increased, when the reaction is carried out in the presence of stannic chloride (catalyst) as illustrated by the reaction of isoprene with methyl vinyl ketone.

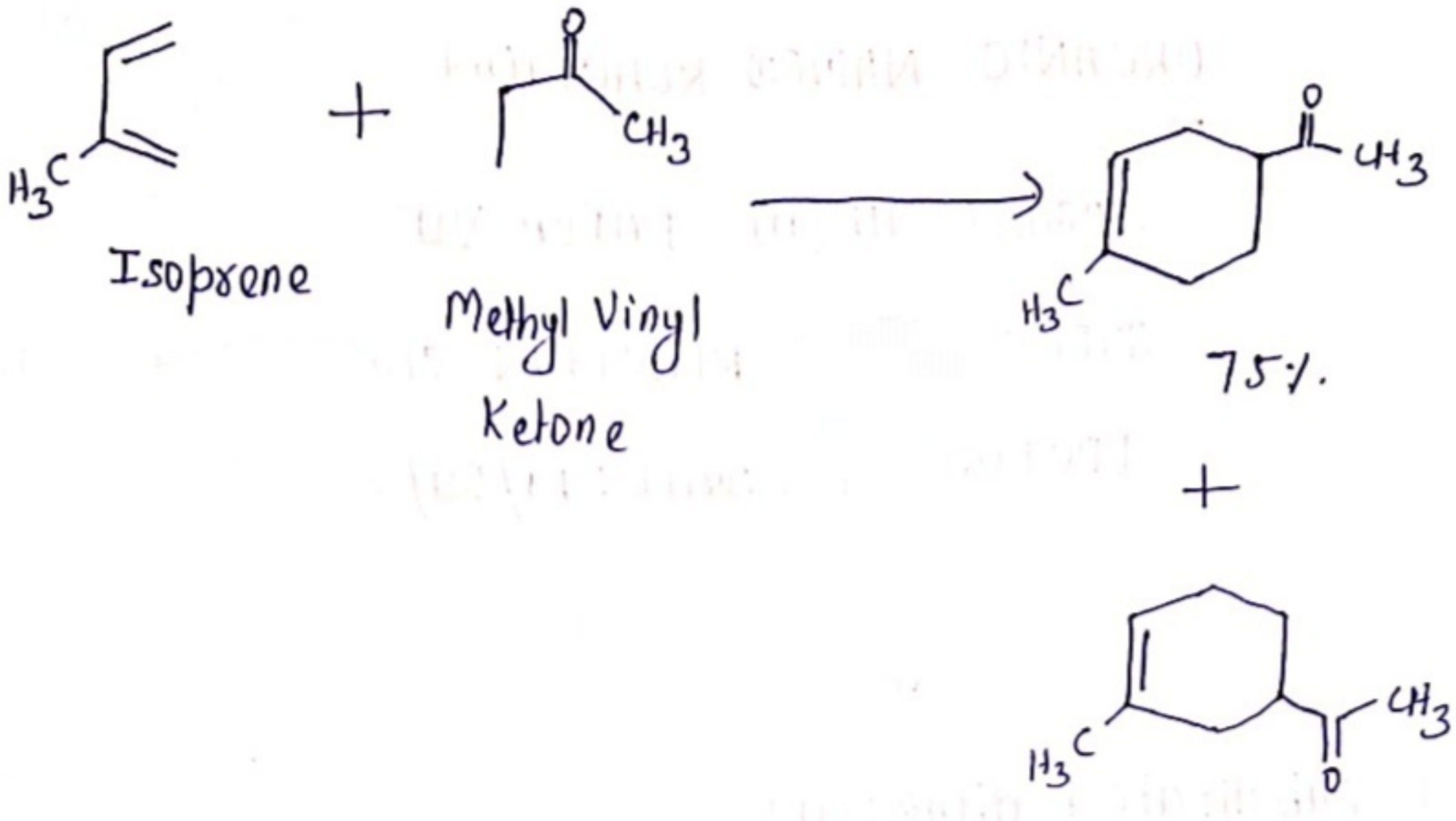


(1) (68%)



(2) (93%)

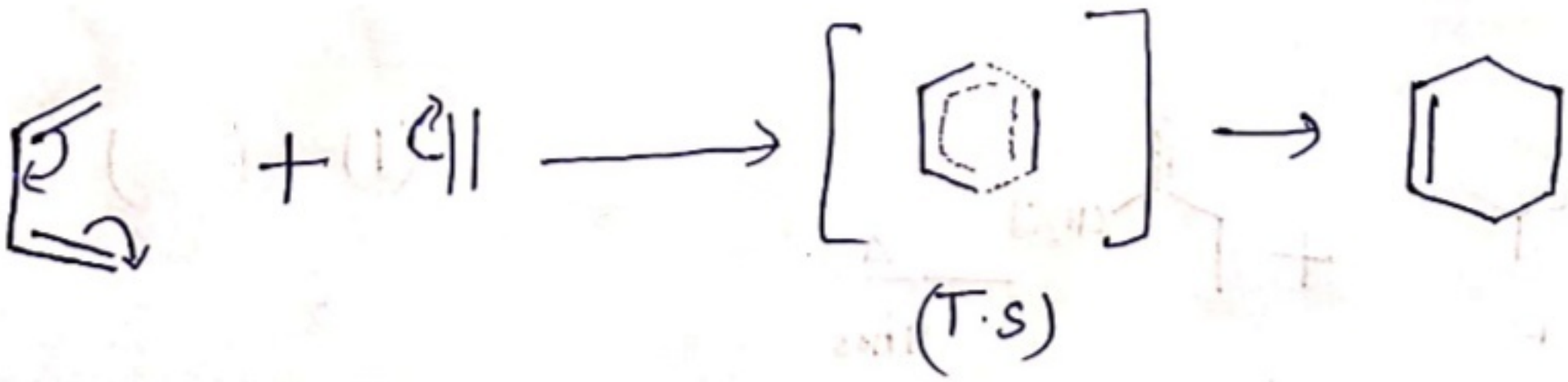
2.



MECHANISM

It is belived that the thermal Diel's-Alder reaction is a concerted addition. In the cyclic transition state, the bond-formation and bond breaking takes place simultaneously, but may not to the same extent.

Such a mechanism is known as retarted concerted mechanism.



The above concerted mechanism for the Diel's-Alder reaction is supported by the following facts.

(i) The reaction is not sensitive to polarity of the solvent and catalyst suggesting thereby the absence of charged transition state or charged intermediate.

(ii) The stereochemistry of the dienophile is preserved in the product, This stereospecificity indicates that both new bonds are formed in the same transition state.

Application

1. Detection of conjugated double bond :---

As the maleic anhydride (dienophile) adds on the conjugated double bonds to form a crystalline adduct, it is a positive test for detecting the presence of a conjugated system in unsaturated compounds.

Thus Diel's - Alder reaction has been successfully used for detecting the conjugated system of double bonds in various natural products viz. vitamin - A, β- Carotene, ergosterol, abietic acid, zinziberene etc.

2. Separation of anthracene and phenanthrene

Since anthracene, but not phenanthrene, forms an adduct with maleic anhydride (addition occurs at the most reactive C_9 & C_{10} position of anthracene) Diel's - Alder Reaction is utilized for the separation of anthracene from phenanthrene.

Anthracene + Phenanthrene $\xrightarrow{\text{Maleic anhydride}}$ Adduct of anthracene

$\downarrow$ Heat in vacuum

Anthracene.

To be continued in next lecture...

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