MILAGRES COLLEGE

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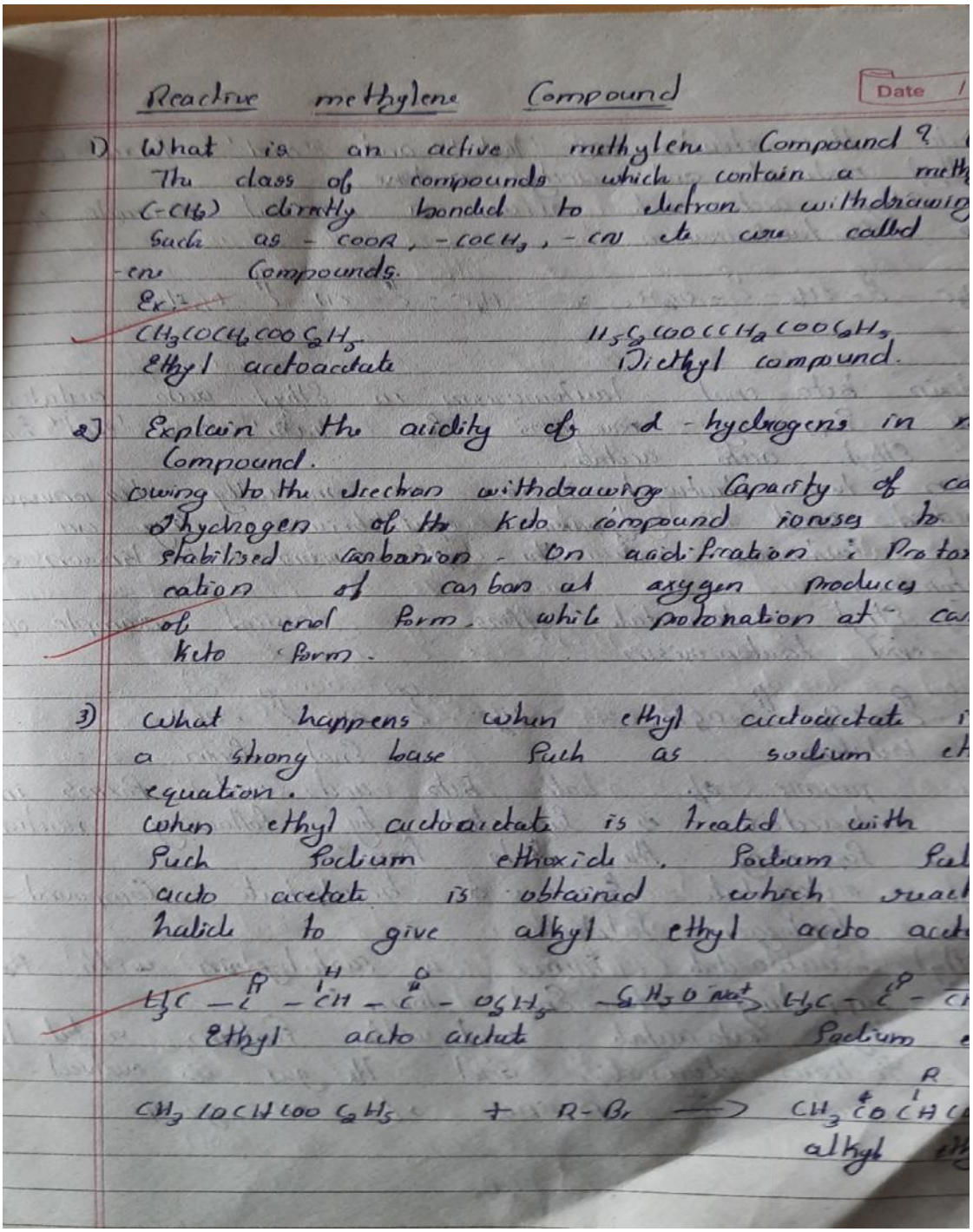
Slow learners Assignment sample copy



Reactive methylene Compound

Date

1) What is an active methylene Compound ?
The class of compounds which contain a meth
(-CH2) directly bonded to electron withdrawing
such as -COOR, -COCH3, -CN etc are called
-CH2 Compounds.
Ex:-
$CH_3COCH_2COOC_2H_5$ $H_5C_2OOCCH_2COOC_2H_5$
Ethyl acetoacetate Diethyl compound.

2) Explain the acidity of α-hydrogens in
Compound.
owing to the electron withdrawing capacity of
Hydrogen of the keto compound ionises to
stabilised carbanion. On acidification : Prot
cation of carbon at oxygen produces
of enol form, while protonation at ca
keto form.

3) What happens when ethyl acetoacetate
a strong base such as sodium
equation.
when ethyl acetoacetate is treated with
such Sodium ethoxide. Sodium Sal
aceto acetate is obtained which react
halide to give alkyl ethyl aceto acet

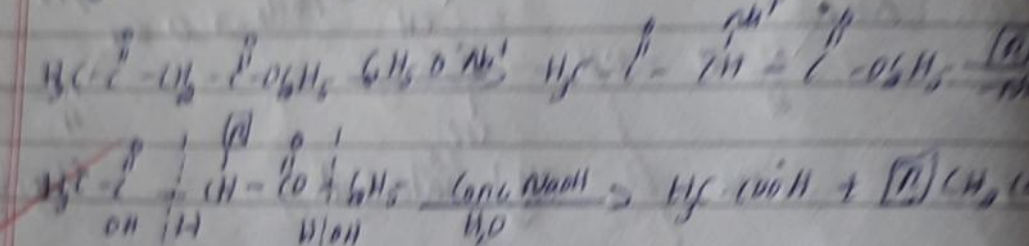
$H_3C-\overset{R}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5ONa} H_3C-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H$
Ethyl aceto acetate Sodium

$CH_3COCH_2COOC_2H_5 + R-Br \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\overset{R}{\underset{|}{C}}HC$
alkyl

2) How are the following synthesized from reactive methylene compounds:

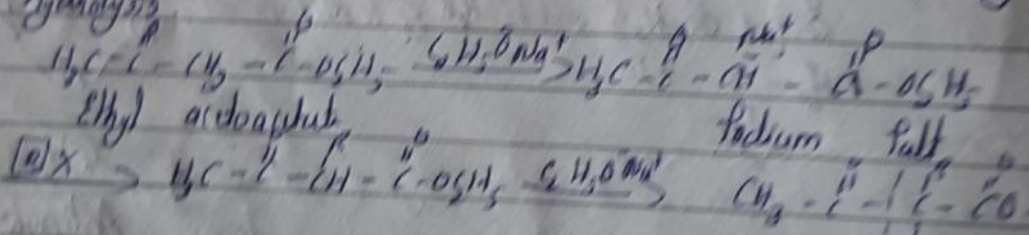
i) Alkyl acetic acid:

This involves the reaction of sodium ethyl acetoacetate with an alkyl halide (RX) followed by acid hydrolysis



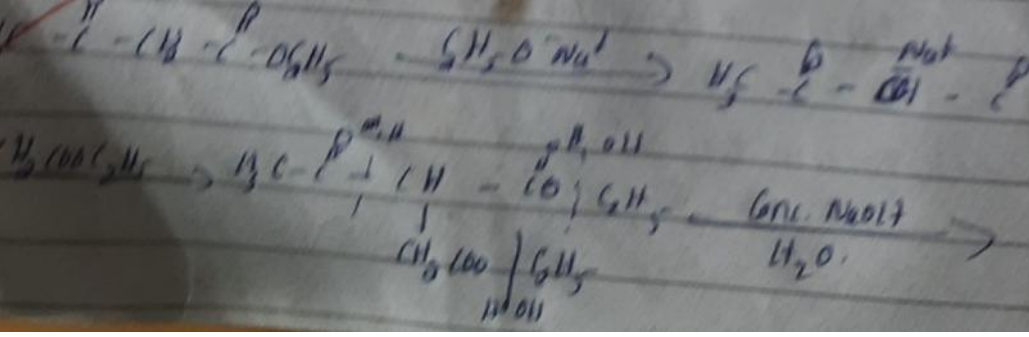
ii) Synthesis of Dialkyl acetic acids:-

Alkylation of sodium ethyl acetoacetate is first with RX and then with R'X followed by acid hydrolysis



iii) Synthesis of Succinic acid:

The reaction of sodium ethyl acetoacetate with ethyl chloroacetate ($ClCH_2COOC_2H_5$) followed by acid hydrolysis gives Succinic acid.



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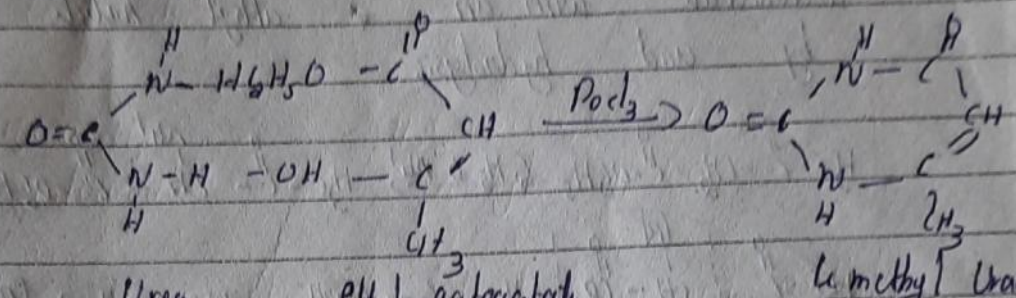
2) How are the following Synthesized?

i) 4-methyl uracil.

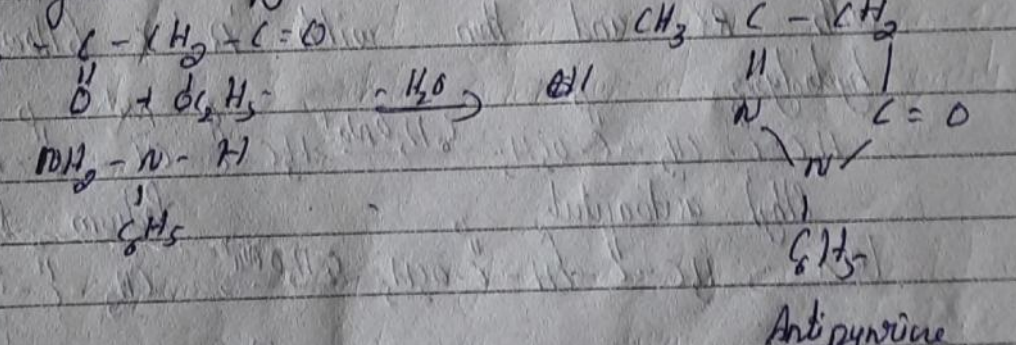
Ethyl acetoacetate reacts with Urea in the presence of phosphoryl chloride to give 4-Methyl Uracil



Urea Ethyl acetoacetate 4-methyl Uracil

ii) Synthesis of Antipyrine:

Ethyl acetoacetate react with Phenyl hydrazine to give Antipyrine



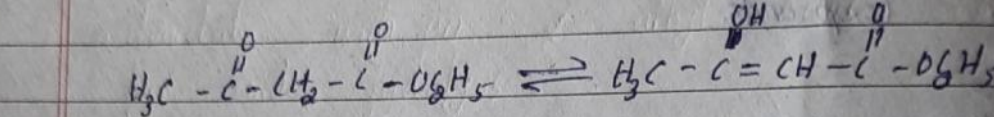
Antipyrine

incomplete

Please write the answers to all question and submit

4) Write the structure of 'keto' and 'enol' forms of diethyl malonate and acetyl acetone.

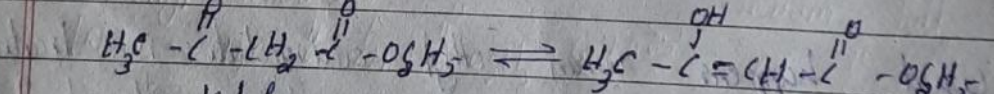
Ethyl acetoacetate offers a classical example of keto-enol tautomerism.



5) Explain keto enol tautomerism in Ethyl aceto acetate. Write supporting reactions for 'keto' and 'enol' form of Ethyl aceto acetate.

When two structural isomers are mutually interconvertible and exist in dynamic equilibrium they are called Tautomers and the phenomenon is known as Tautomerism.

Ethyl aceto acetate offers a classical example of keto-enol tautomerism



Ketoform Enol form.

The presence of both keto and enol forms in ethyl acetoacetate is supported by following reactions

Reaction supporting the keto form:-

1) Ethyl acetoacetate forms a bisulphate compound with Sodium hydrogen Sulphate.

2) Ethyl acetoacetate forms a carbohydrin with HCN.

Reaction supporting the Enol form:-

1) The ethyl aceto acetate react with Sodium metal to form Sodium derivative and H_2 gas is evolved. This indicates the presence of OH group.

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$CH_3COOH + C_6H_5OH + CH_3COOH$ (Formic acid)

Synthesis of keto acids :-

This involves the reaction of sodium diethyl malonate with acid halids followed by hydrolysis and decarboxylation.

$H_2C(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa^+} Na^+CH(COOC_2H_5)_2 \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-Cl}$

$CH_3-\overset{O}{\overset{\|}{C}}-CH(COOC_2H_5)_2 \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH(COOH)_2 \xrightarrow{heat}$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOH$

Synthesis of α, β unsaturated acids :-

Base catalysed reaction ethyl acetoacetate with an aldehyde or ketone followed by hydrolysis gives α, β - unsaturated acids.

$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{(C_2H_5)_2NH} CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3-C-H}{\overset{\overset{H}{|}}{C}}-CO + C_2H_5OH$

$\xrightarrow{Conc.\ NaOH} CH_3COOH + C_2H_5OH + CH_3CH=CHCOOH$

Crotonic acid.

Ch 20/5/2020

Principal

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