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REACTION PATHWAYS of CARBOXYLIC ACID DERIVATIVES

Peter Sykes



ETSG

CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

General Editor:
Peter Groves
The University of Aston in Birmingham

Published 1979 by the Educational Techniques Subject Group, The Chemical Society, London.

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ISBN 0 85186 640 9

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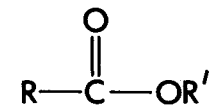
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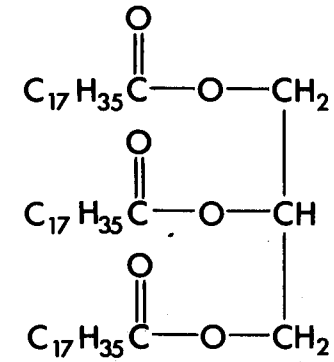
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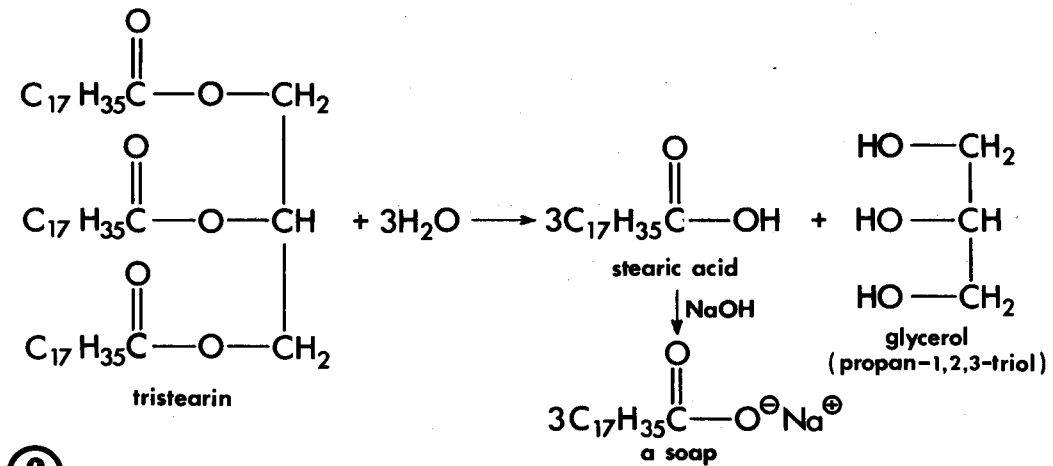
①

STRUCTURE OF AN ESTER



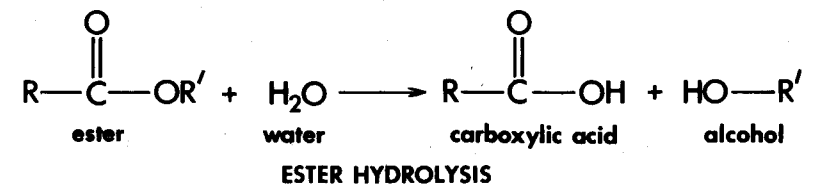
②

A TYPICAL FAT : TRISTEARIN (BEEF FAT)

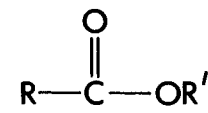


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SAPONIFICATION (HYDROLYSIS) OF A FAT

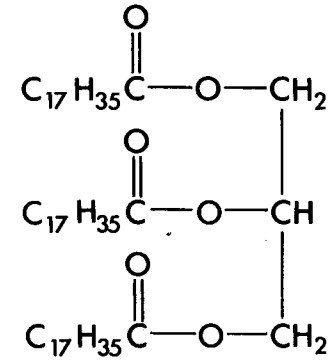


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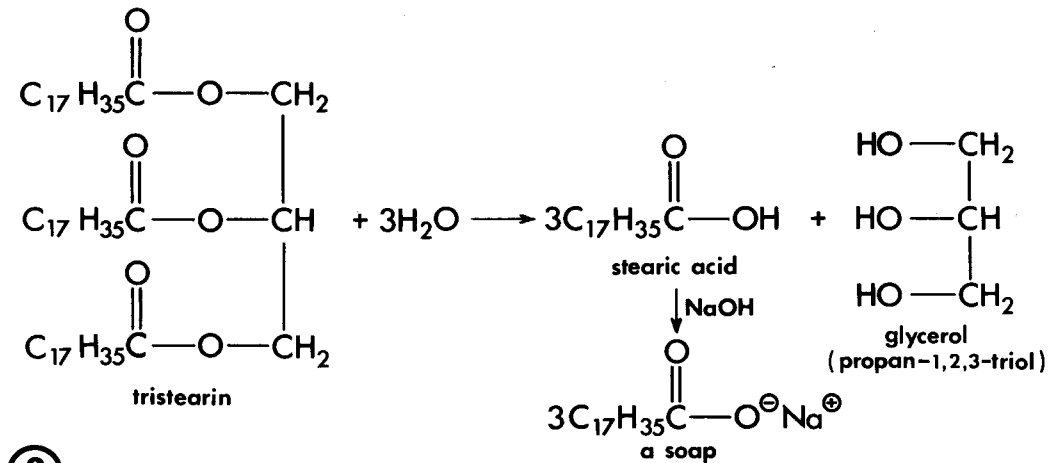
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STRUCTURE OF AN ESTER



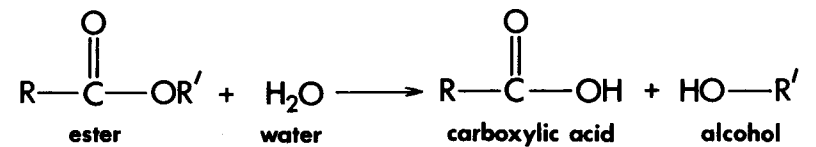
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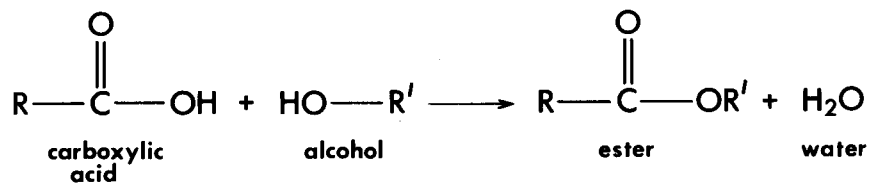
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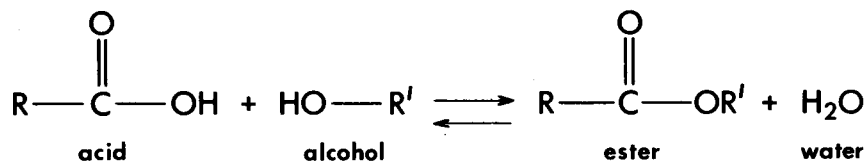


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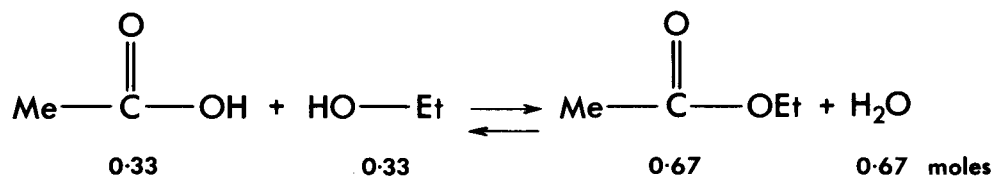
ESTER HYDROLYSIS



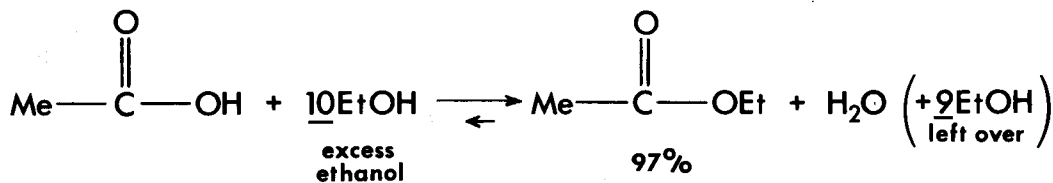
5 ESTER FORMATION : ESTERIFICATION



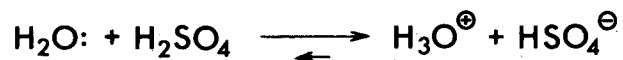
6 ESTERIFICATION/HYDROLYSIS : EQUILIBRIUM



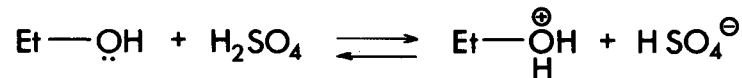
7 EQUILIBRIUM POSITION : ESTERIFICATION/HYDROLYSIS



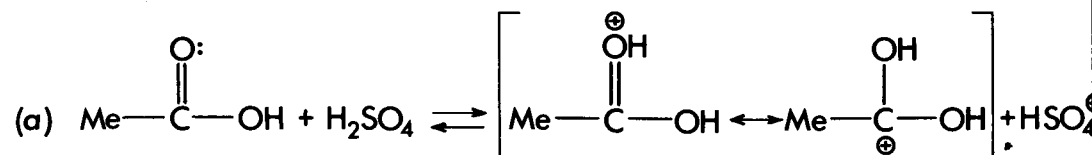
8 EQUILIBRIUM POSITION : EXCESS EtOH



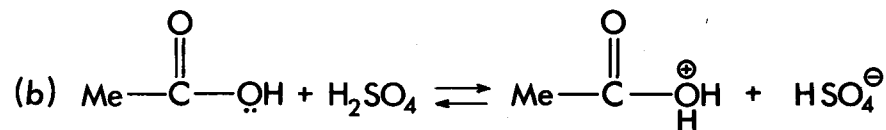
9 PROTONATION OF H₂O: BY H₂SO₄



10 PROTONATION OF EtOH BY H₂SO₄

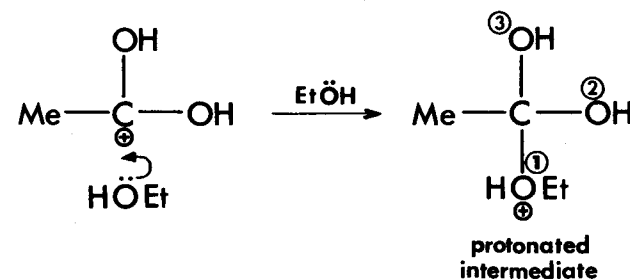


✓ carbonyl oxygen protonation

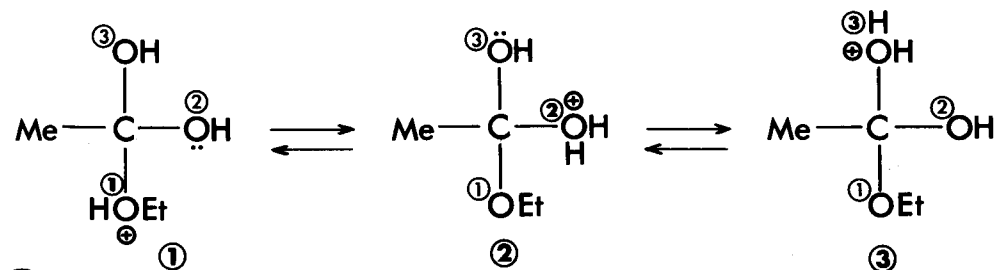


✗ hydroxyl oxygen protonation

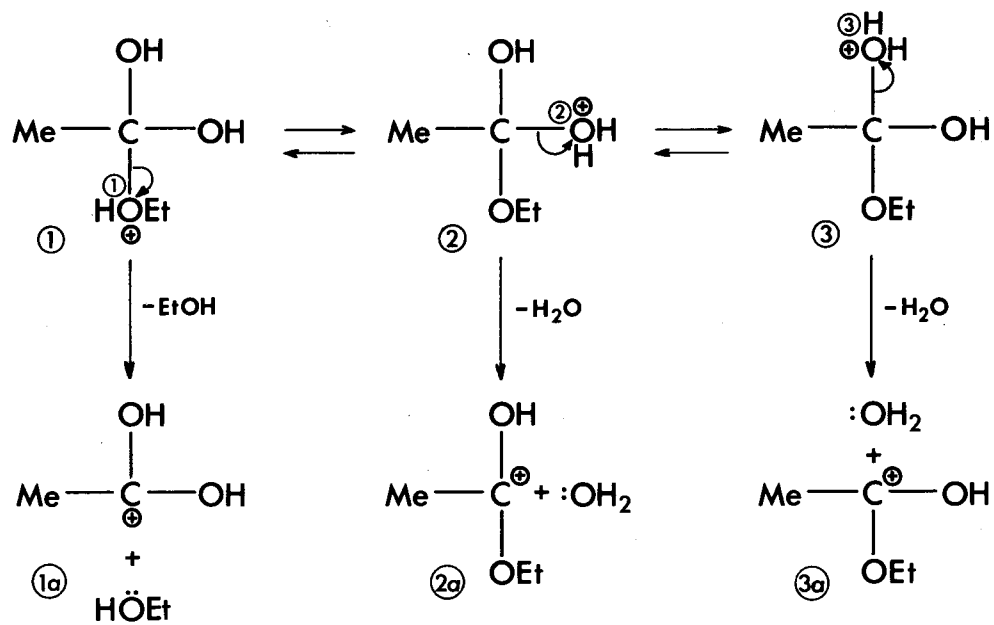
11 ALTERNATIVE POSSIBLE PROTONATIONS OF ETHANOIC ACID



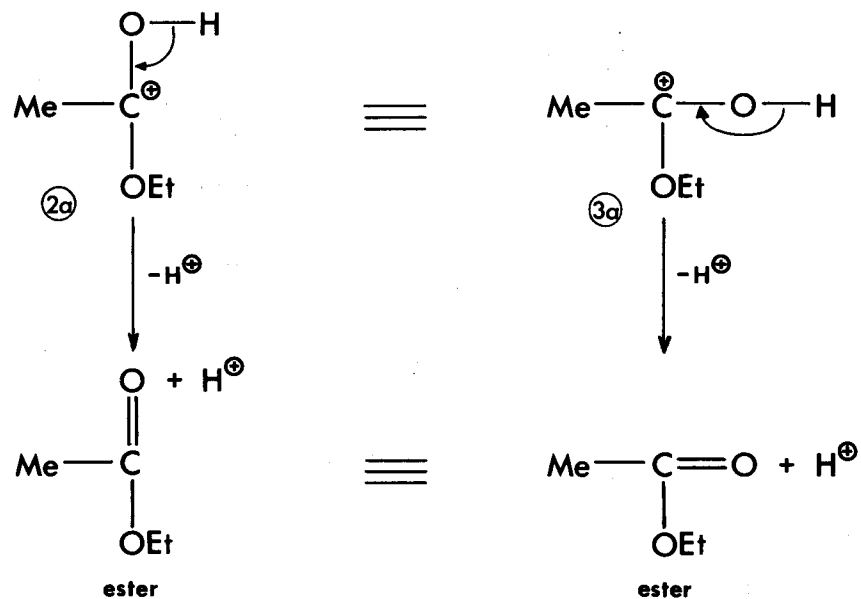
12 EtOH ATTACKING PROTONATED ACID



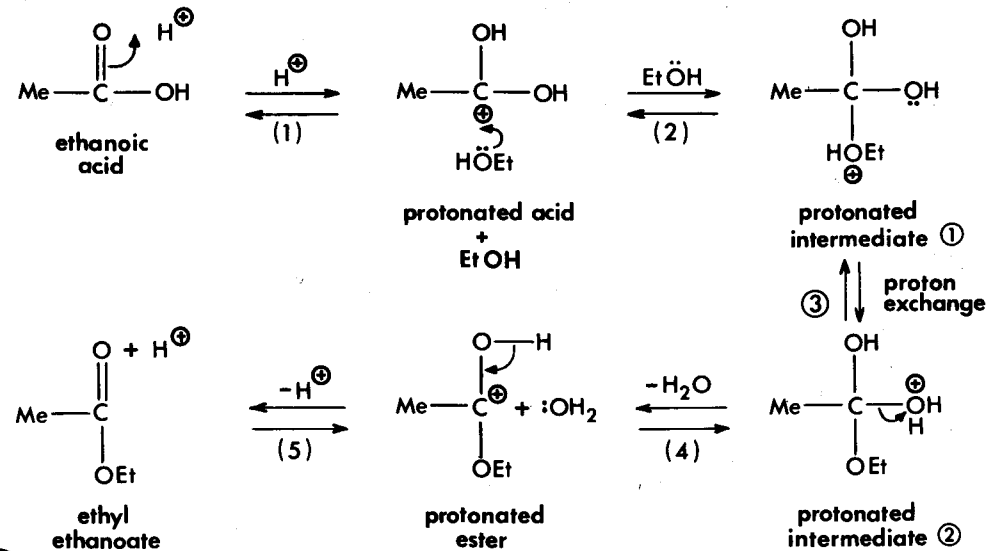
13 PROTON EXCHANGE IN PROTONATED INTERMEDIATES



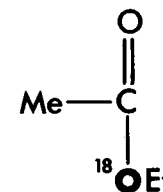
14 LOSS OF LEAVING GROUP FROM PROTONATED INTERMEDIATES



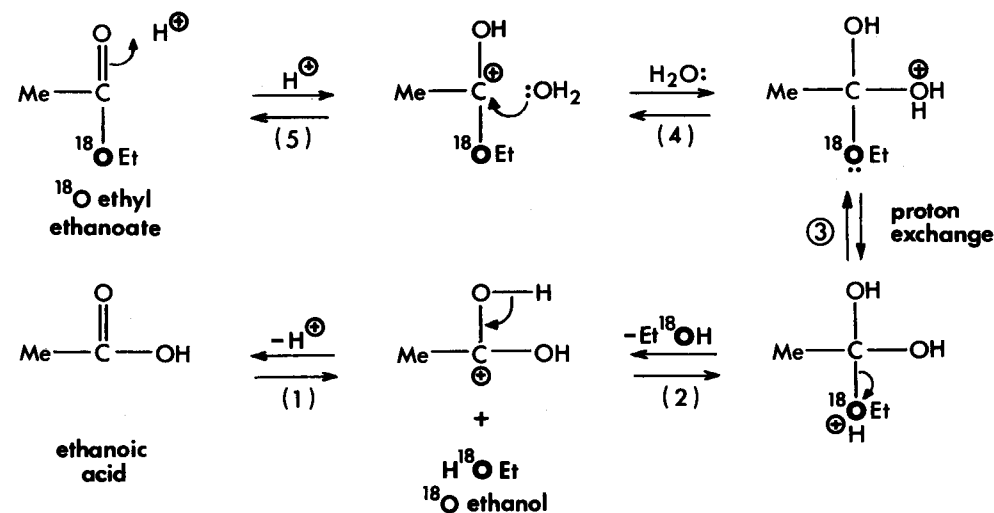
15 FINAL LOSS OF PROTON TO FORM ESTER



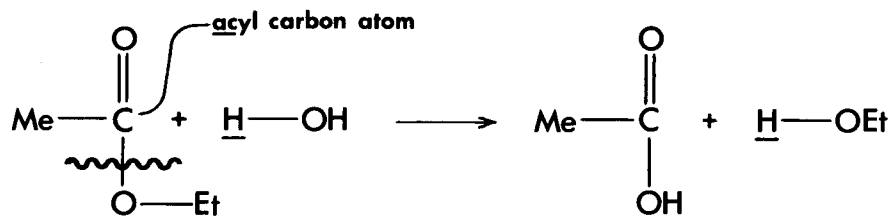
16 ACID-CATALYSED ESTER FORMATION/HYDROLYSIS



17 ETHYL ETHANOATE: ¹⁸O LABELLED AT ALKYL OXYGEN

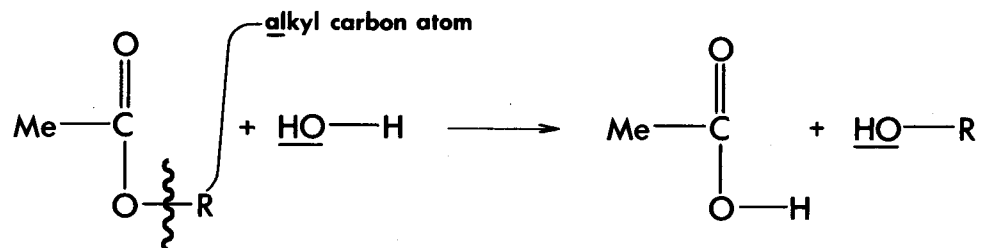


18 HYDROLYSIS OF ¹⁸O LABELLED ESTER → H¹⁸OEt



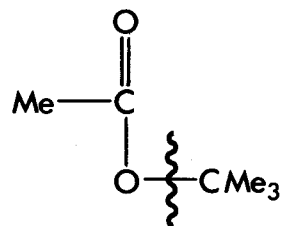
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ACYL/OXYGEN (AC) CLEAVAGE OF ESTERS



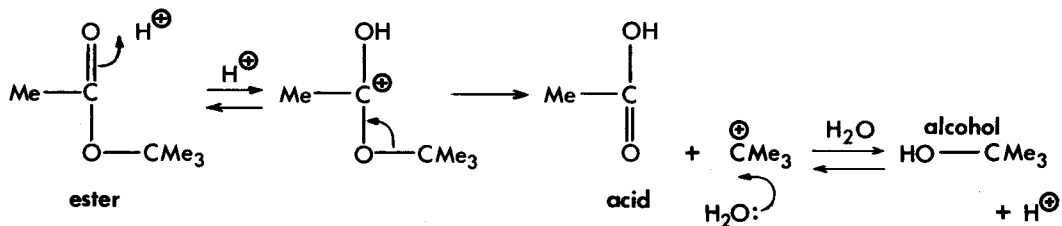
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ALKYL/OXYGEN (AL) CLEAVAGE OF ESTERS



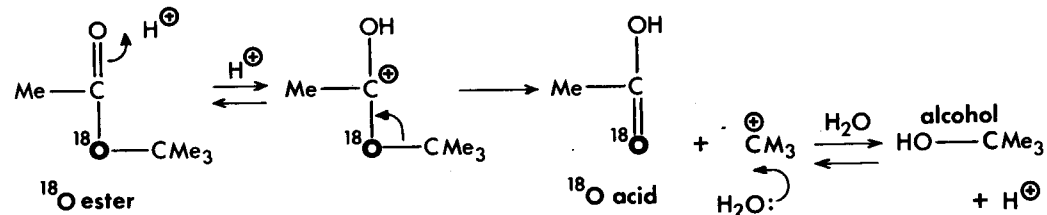
21

ALKYL/OXYGEN (AL) CLEAVAGE OF t-BUTYL ESTER



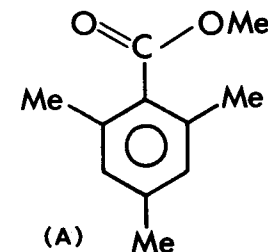
22

POSSIBLE ALKYL/OXYGEN (A_{AL}) HYDROLYSIS PATHWAY



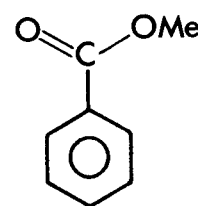
23

A_{AL} HYDROLYSIS OF ¹⁸O LABELLED ESTER → Me-¹⁸O-C-OH

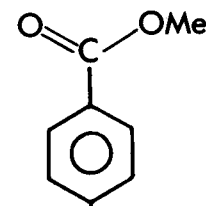


24

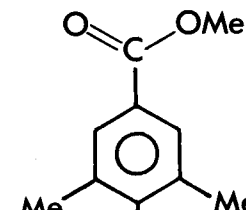
METHYL ESTER (A) OF AN AROMATIC ACID



(B)



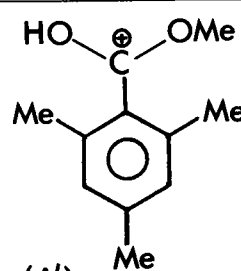
(C)



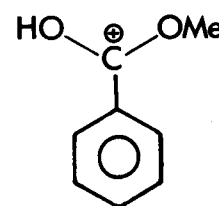
(D)

25

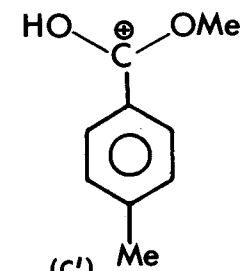
METHYL ESTERS OF THREE MORE AROMATIC ACIDS



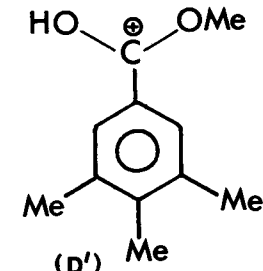
(A')



(B')



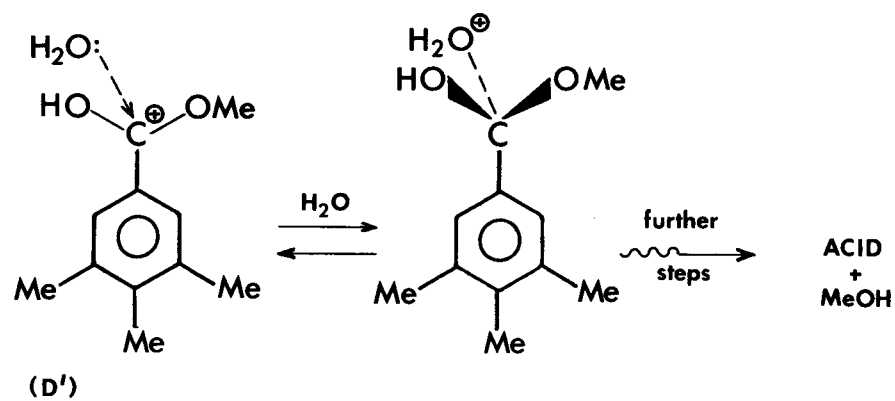
(C')



(D')

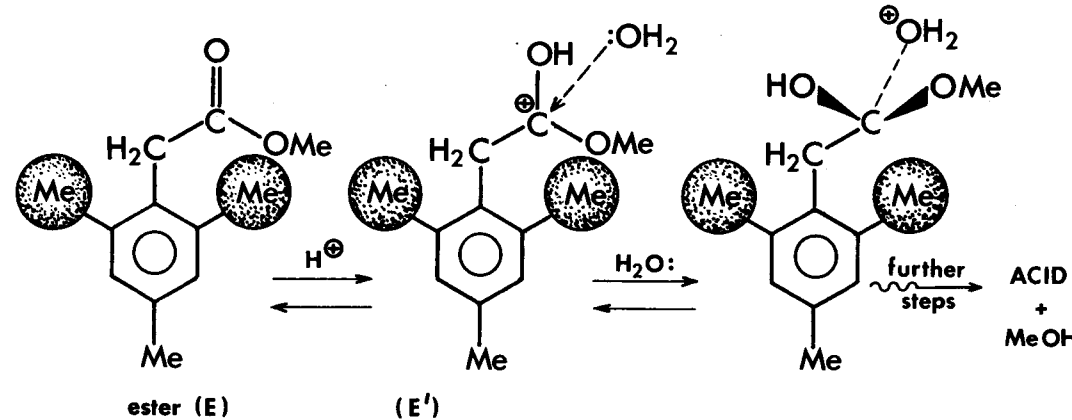
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PROTONATED FORMS OF ALL FOUR ESTERS



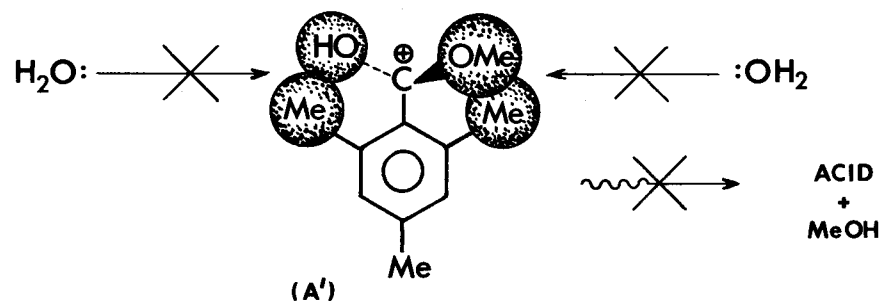
27

H₂O: ATTACK ON PROTONATED ESTER (D')



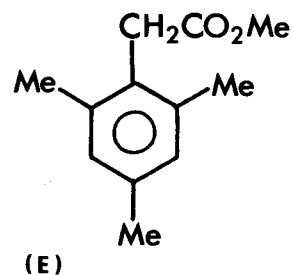
30

ACID HYDROLYSIS OF ESTER (E)



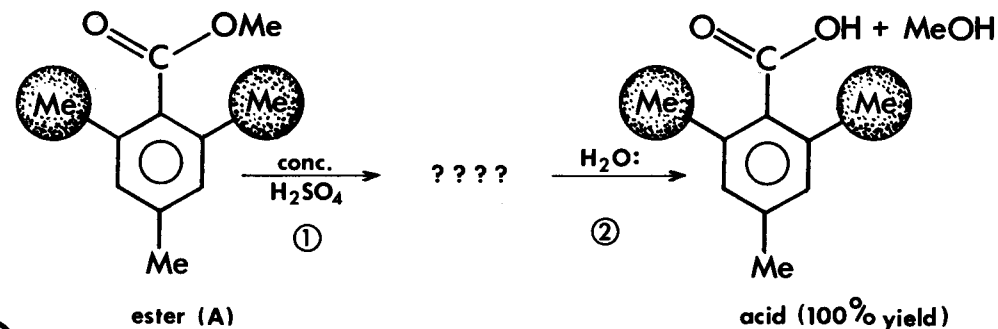
28

NO H₂O: ATTACK ON PROTONATED ESTER (A')



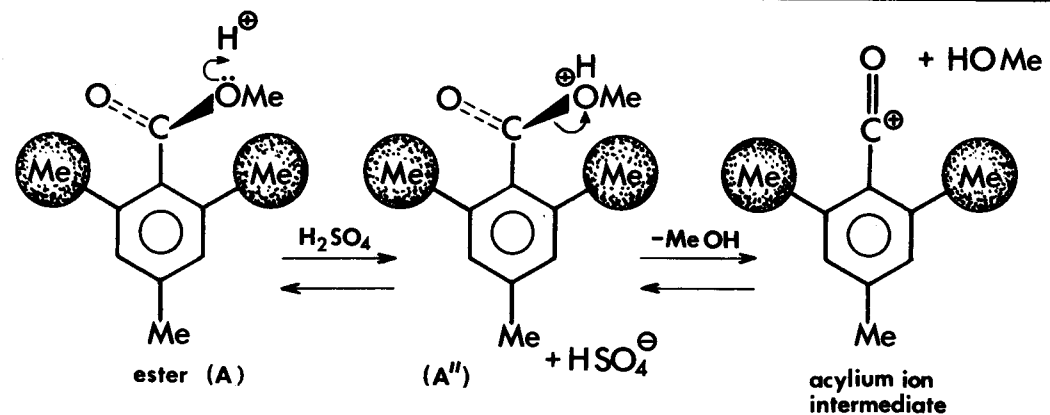
29

METHYL ESTER (E) OF YET ANOTHER AROMATIC ACID!



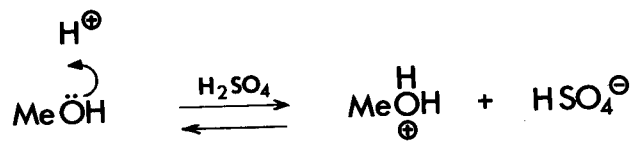
31

ACID HYDROLYSIS (CONC H₂SO₄) OF ESTER (A)

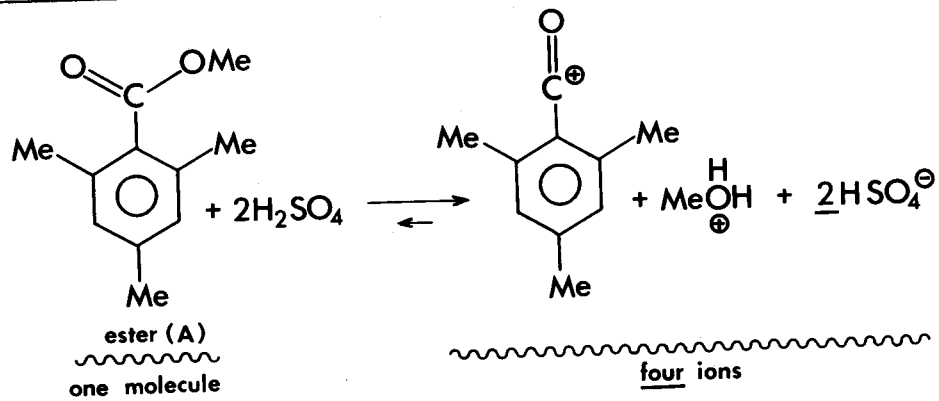


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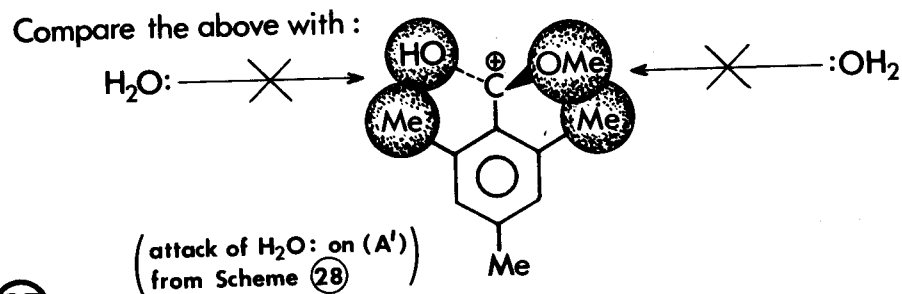
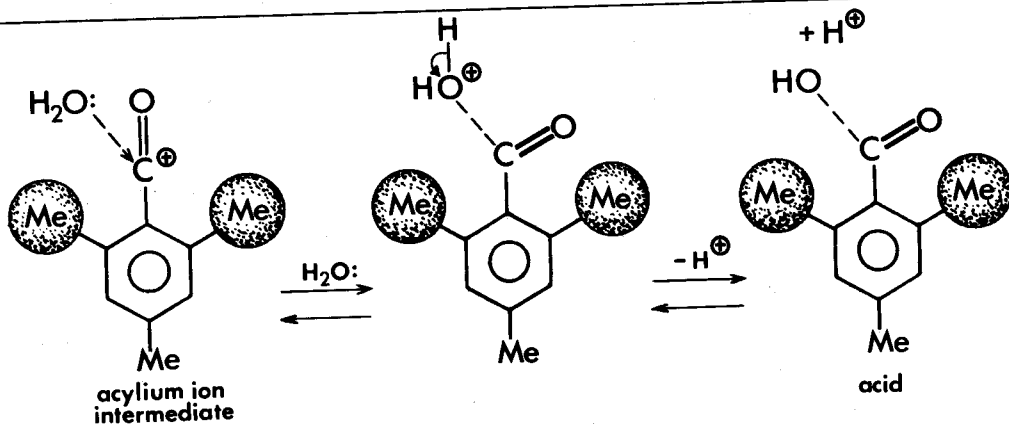
ACYLIUM ION INTERMEDIATE FROM ESTER (A)



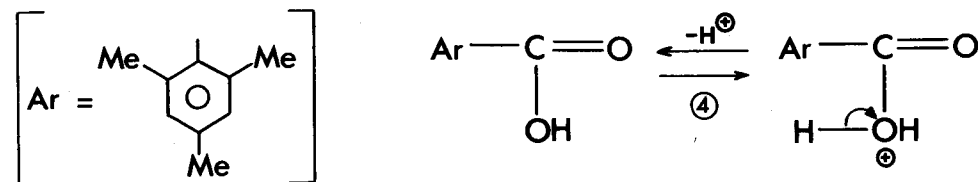
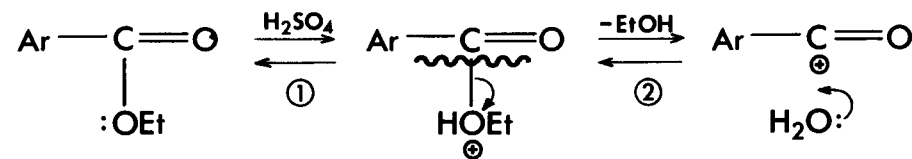
PROTONATION OF MeOH



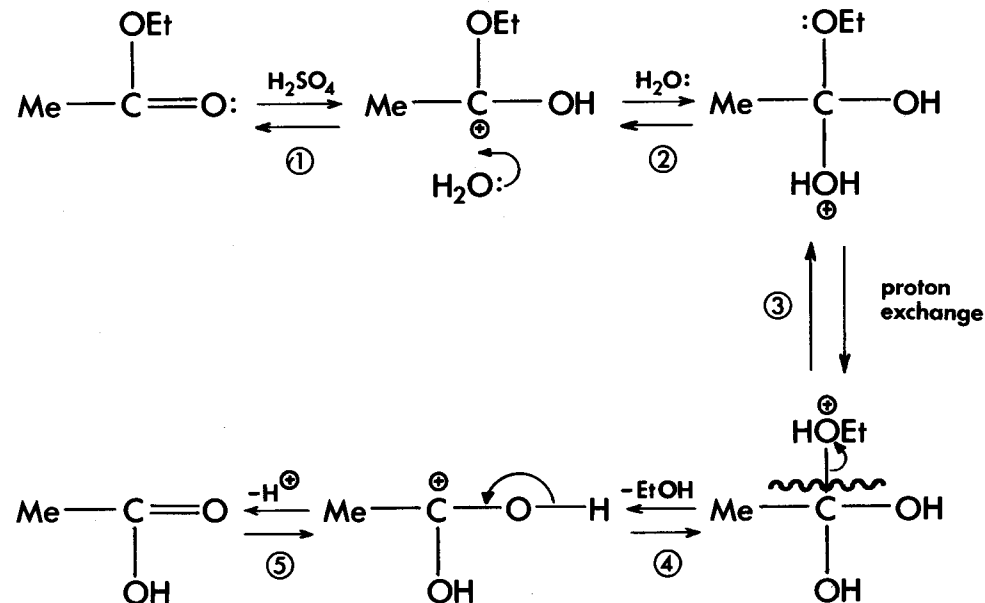
ESTER (A) + CONC. H₂SO₄ → FOUR IONS



ATTACK OF H₂O: ON ACYLIUM ION INTERMEDIATE



(i) A_{AC} : PATHWAY X



(ii) A_{AC} : PATHWAY Y

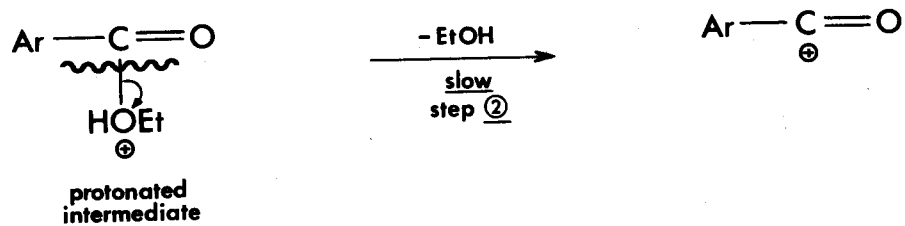
A_{AC} HYDROLYSIS: (i) AROMATIC ESTER; (ii) ETHYL ETHANOATE

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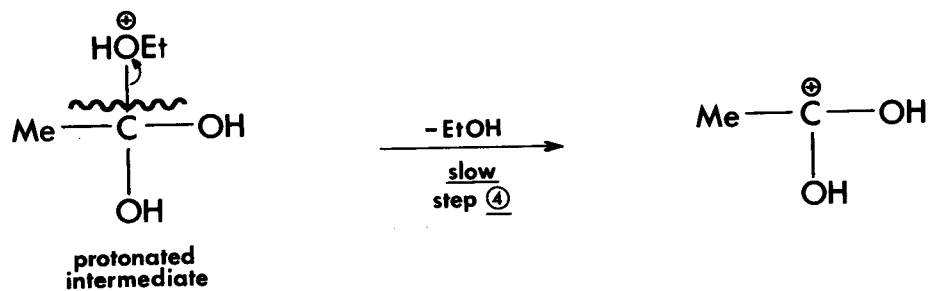
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36



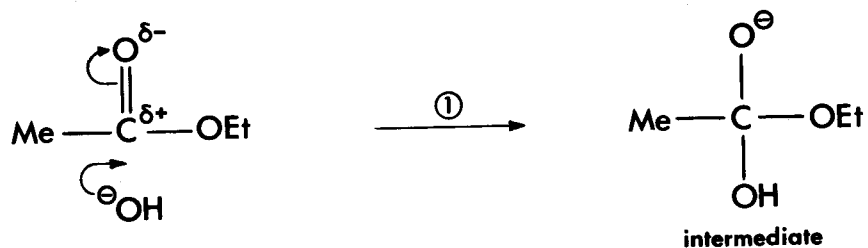
PATHWAY X: A_{AC}1



PATHWAY Y: A_{AC}2

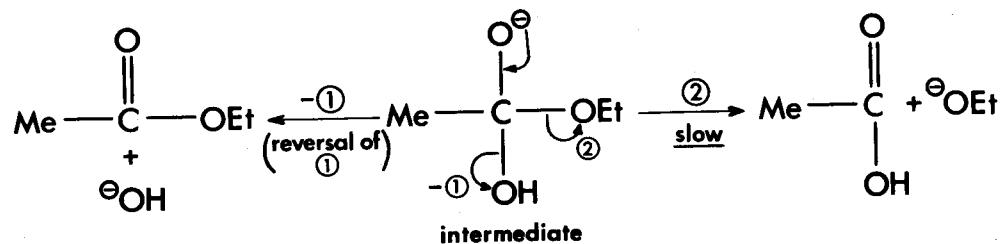
RATE-LIMITING STEPS: PATHWAYS X(A_{AC}1) AND Y(A_{AC}2)

37



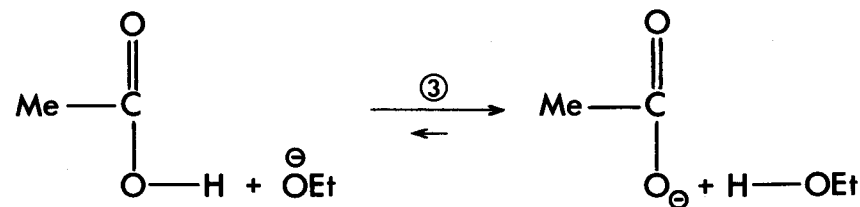
NUCLEOPHILIC ATTACK BY OH^- ON $\text{C}=\text{O}$ IN ESTER

38



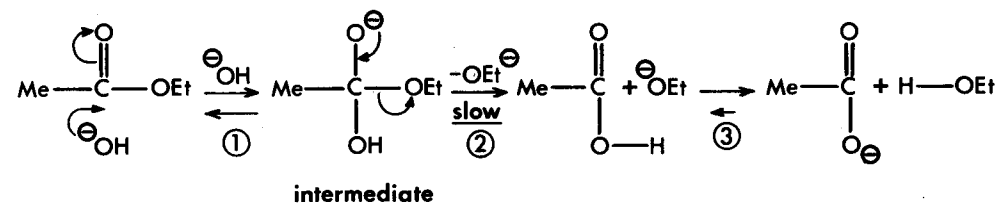
POSSIBLE FATES OF NEGATIVELY CHARGED INTERMEDIATE

39



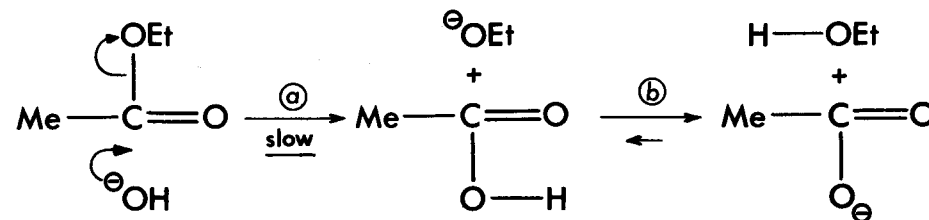
MeCO₂H v. EtOH : STRENGTHS AS ACIDS

40



BASE-CATALYSED ESTER HYDROLYSIS : B_{AC}2 PATHWAY

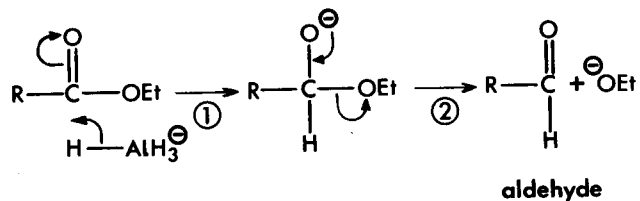
41



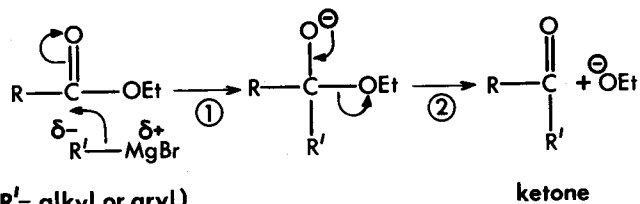
HYDROLYSIS BY DIRECT DISPLACEMENT PATHWAY

42

(i) LiAlH_4 :



(ii) $\text{R}'\text{MgBr}$:

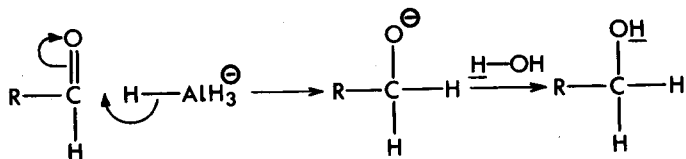


($\text{R}' = \text{alkyl or aryl}$)

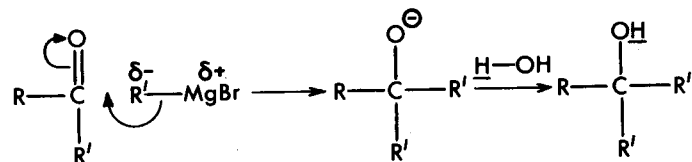
50

NUCLEOPHILIC ATTACK BY LiAlH_4 AND $\text{R}'\text{MgBr}$

(i) LiAlH_4 (cont):



(ii) $\text{R}'\text{MgBr}$ (cont):



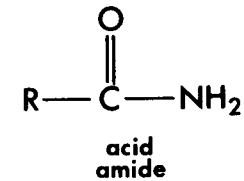
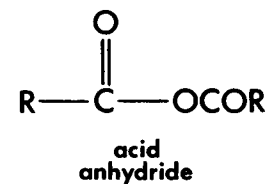
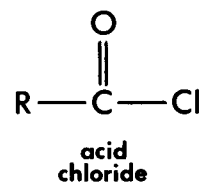
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CONTINUATION OF NUCLEOPHILIC ATTACK

Reagent added:	NaCl	NH_3	NaOH	LiAlH_4	RMgBr
Potential nucleophile:	Cl^\ominus	$:\text{NH}_3$	$^\ominus\text{OH}$	AlH_4^\ominus	R^\ominus
Relative basic strength: (log scale)	1	10	15	≈ 40	≈ 40

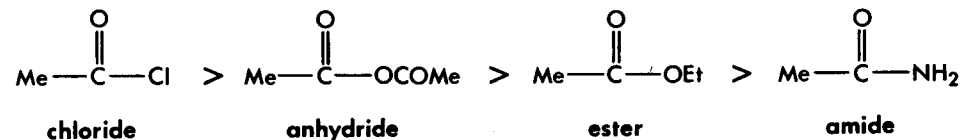
52

RELATIVE BASIC STRENGTH OF SOME NUCLEOPHILES



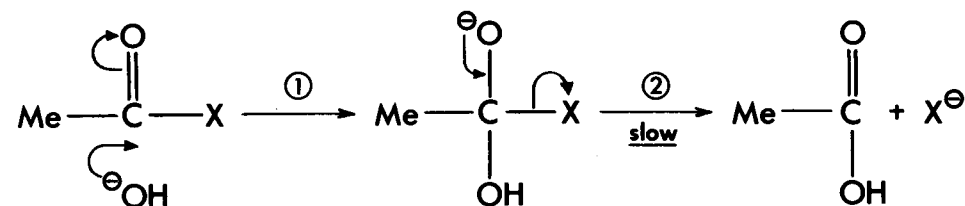
53

SOME OTHER CARBOXYLIC ACID DERIVATIVES



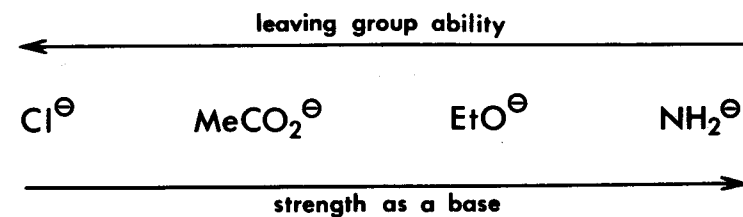
54

RELATIVE REACTIVITY OF ETHANOIC ACID DERIVATIVES



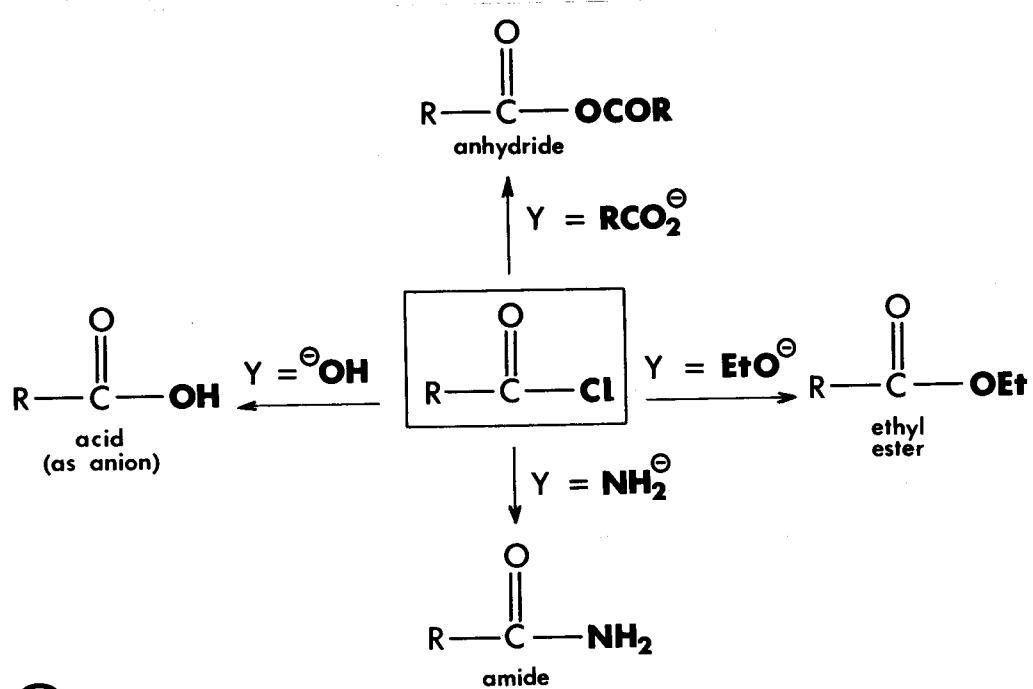
55

REACTION OF $^\ominus\text{OH}$ WITH $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$



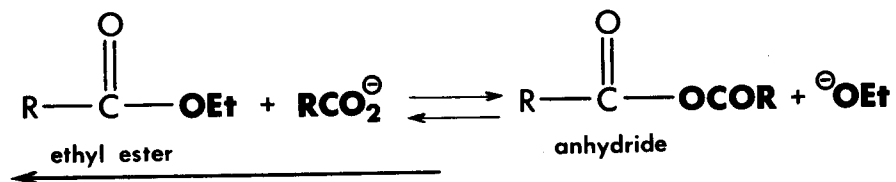
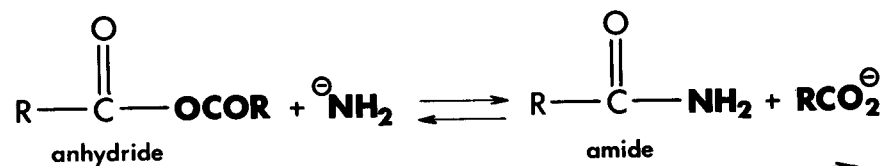
56

RELATIVE LEAVING GROUP ABILITY / BASIC STRENGTH OF X^\ominus



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NUCLEOPHILIC REPLACEMENTS OF Cl^\ominus IN RCOCl



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INTERCONVERSIONS OF CARBOXYLIC ACID DERIVATIVES

