20.3 Baeyer-Villiger Reaction (Rearangers) est.)

The reaction consists in the oxidation of a ketone into an ester by means of a peracid.

R2CO + R'COOOH -→ RCOOR + R'COOH Cyclic ketones give lactones.

A number of peracids viz. trifluoroperacetic, peracetic, perbenzoic, monoperphthalic, monopersulphuric acid, etc., have been successfully used in the reaction. But trifluoroperacetic acid is the most reactive among all the above mentioned peracids.

The mechanism of this reaction is believed to involve acid-catalysed addition of the per acid to the ketonic carbonyl group to form an intermediate peroxide, followed by migration of an alkyl group to an electron-deficient peroxide oxygen atom.

It is important to note that in the presence of a strong acid there may be addition of peroxy-acid to the protonated ketone, but additional acid is not needed and in its absence addition may take place to the ketone itself. The general mechanism is supported by the fact that the reaction is catalysed by acid and is accelerated by electron-releasing groups in the ketone and by electron with drawing groups in the peracid. Further that the oxygen atom of the carbonyl group of the ketone is the same one as in the carbonyl group of the ester was clearly demonstrated by the following reaction in which isotopically labelled oxygen (O¹⁸) is taken in the molecule.

$$C_6H_5$$
— $C_+C_6H_5$ C_6H_5 C_6H_5 C_6H_5 C_6H_5

During the mechanism it is observed that an alkyl group migrates from carbon to oxygen; the order of this migratory aptitude in the alkyl series is tertiary > secondary > primary [Fries; 1950], e.g.

Among the aryl series the order is: p-anisyl > p-tolyl > p-chlorophenyl > p-nitrophenyl > p-aminophenyl, etc. [Doering; 1950]. When aryl and alkyl, both groups, are present, the migratory aptitude of various groups is: tertiary alkyl > sec. alkyl, aryl, benzyl > primary alkyl > methyl. Thus in acetophenone, phenyl group migrates in preference to the methyl.

$$C_6H_5$$
.CO.CH₃ \longrightarrow C_6H_5 —O—CO.CH₃

Acetophenone Phenyl acetate

It must be noted that the reaction is intramolecular and thus the migrating group retains its configuration as shown by the fact that optically active 3-phenyl-2-butanone affords optically active α -methylbenzyl acetate.

Applications: 1. The reaction is frequently used for the synthesis of the following types of compounds.

$$R.CO.R' \xrightarrow{RCO,H} R-O.COR' \xrightarrow{HOH} R'COOH + ROH$$

(6) Anhydrides: When α -diketones or α -quinones are treated with peracids, anhydrides are produced, e.g.,

1, 2-Naphthaquinone

(f) Lactones: Cyclic ketones undergo ring expansion with peracids, e.g., cyclohexanone gives e-caprolactone.

Cyclobexapone

e- Caprolactone

By this method lactones containing large rings (fourteen to eighteen membered rings) have been prepared by the oxidation of the respective ketone (Ruzicka and Stoll, 1928).

$$H_2C < (CH_2)_n > CO \xrightarrow{RCO,H} H_2C < (CH_2)_n - CO (CH_2)_n - CO$$

2.The Baeyer-Villeger rearrangement is also useful in the degradation of organic molecules for proof of structure. This is because a carbon-carbon bond is broken and the ester produced can be easily hydrolysed; this divides the molecule into two fragments for easier identification.