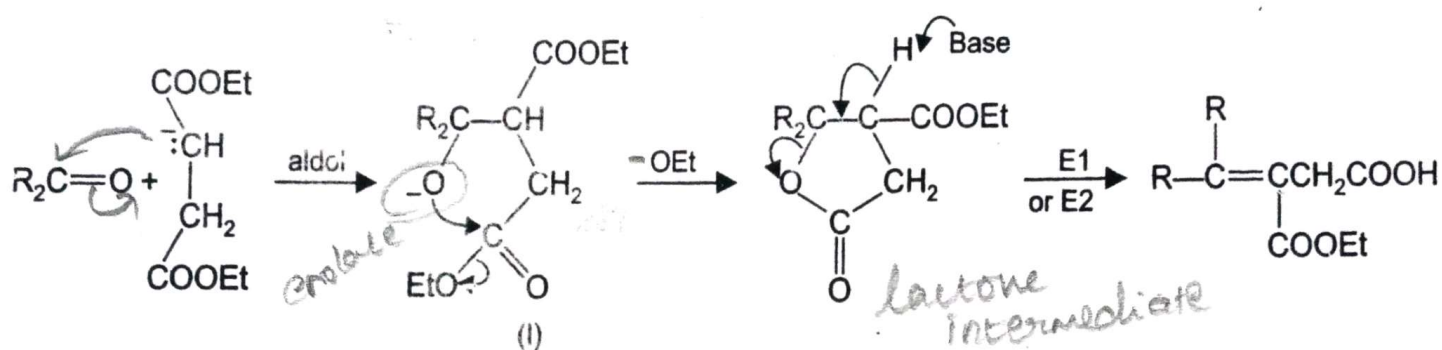


SCHEME 6.24

(I) The Stobbe Condensation ✓

This is a condensation between dialkyl succinates and ketones in the presence of bases like NaOEt. Mechanistically the enolate from the ester adds to the carbonyl group of the ketone (Scheme 6.25). One may compare this situation with that in Claisen ester condensation where in the presence of a base, the enolate from the ketone displaces alkoxide ion from the ester. In the Stobbe condensation, the condensation product (I, Scheme 6.25) undergoes cyclization to give a lactone intermediate, the oxygen anion of the adduct (I, Scheme 6.25) acting as an internal nucleophile facilitates the hydrolysis of one of the ester groups. The lactone then undergoes elimination (E1 or E2) to give a carboxylate salt. The net result is the attachment of a three carbon chain to the ketonic carbon atom.

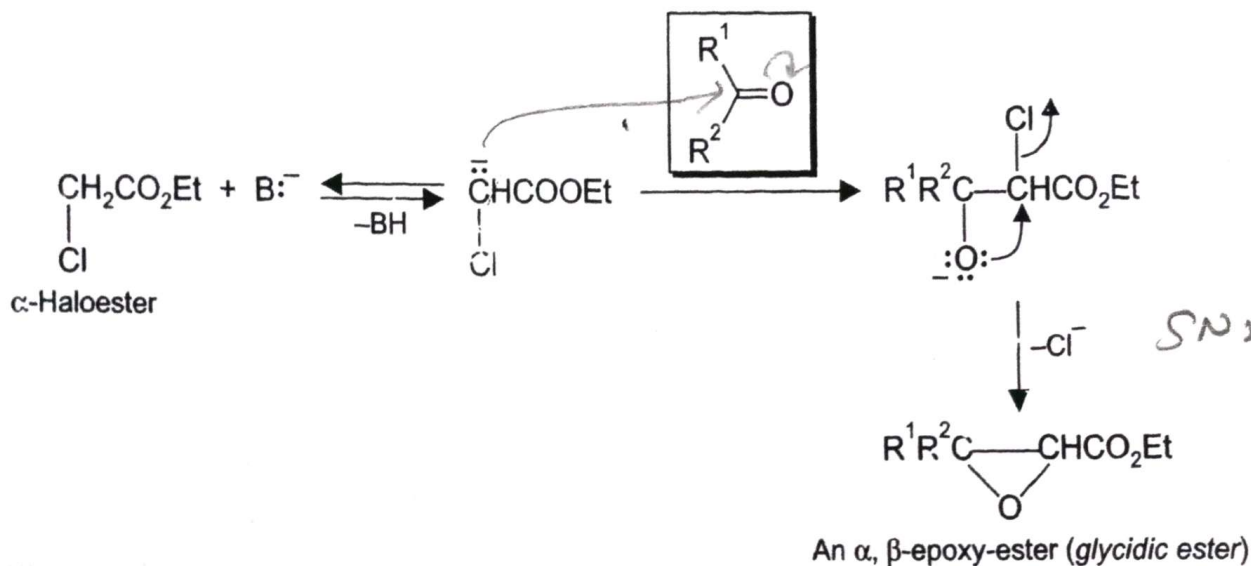


The Stobbe condensation

SCHEME 6.25

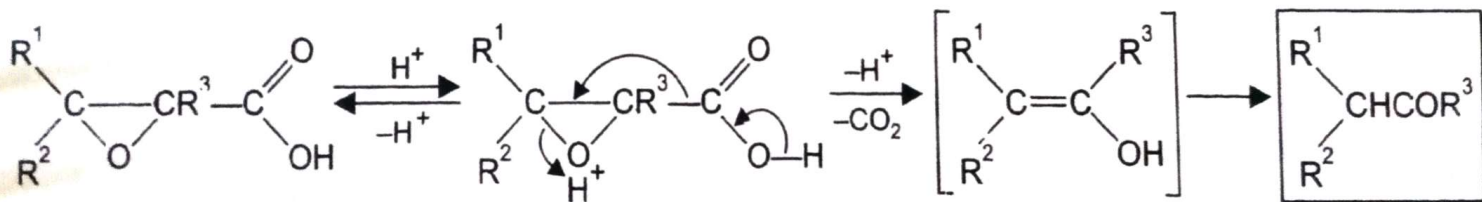
(J) Darzens Reaction ✓

Aldehydes and ketones condense with α -haloesters in the presence of bases to give α, β -epoxy esters called (glycidic esters). The reaction called Darzens condensation involves the addition of the enolate to the carbonyl group to give an oxyanion (Scheme 6.26), this displaces the halide ion by an internal S_N2 reaction. On alkaline hydrolysis, these esters give glycidic acids which undergo a decarboxylative rearrangement when warmed in the presence of acids (Scheme 6.27) to give an aldehyde if $R^3=H$ or a ketone if $R^3=\text{alkyl group}$. Thus the eventual outcome of such a reaction is to extend the chain by one carbon.



The Darzens reaction
 Darzens reaction involves the reaction of an α -halo ester with an aldehyde or a ketone in an aldol type reaction to give a glycidic ester

SCHEME 6.26



SCHEME 6.27

When *t*-butyl glycidates are used, the ester on pyrolysis eliminates isobutene to give an aldehyde or ketone (Scheme 6.28).

