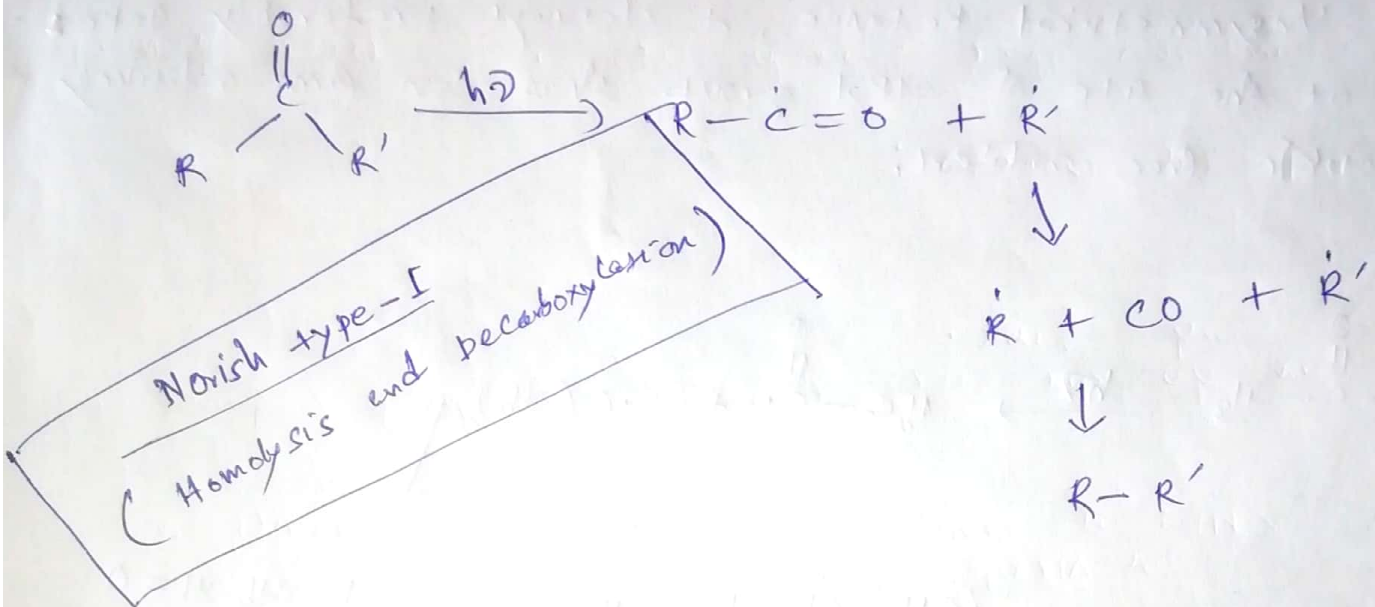


Unconjugated ketones on photo-excitation undergo α -cleavage followed by decarbonylation and subsequent reactions of alkyl radicals to give products.

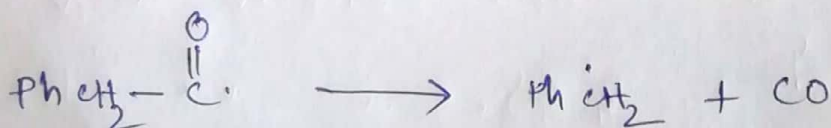
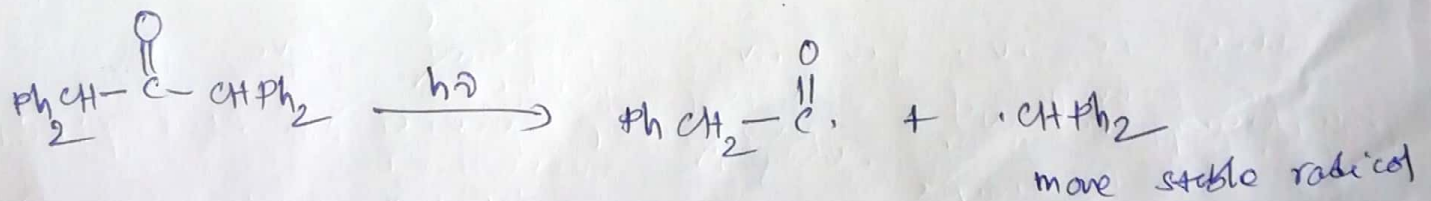
All these processes are collectively known as Norish-type-I cleavage reactions. These reactions take place both in gaseous and liquid phases.

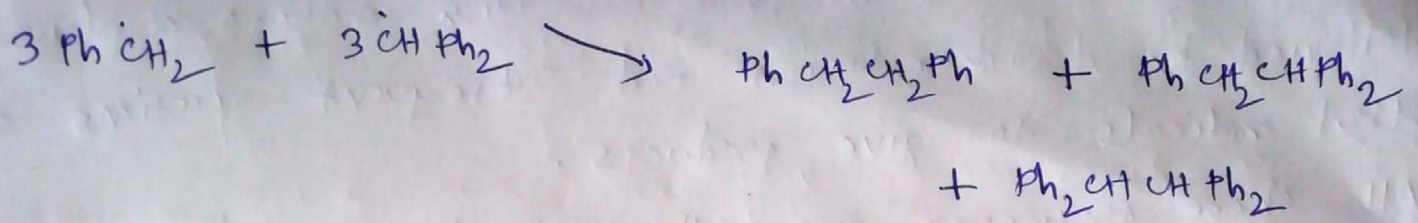


The energies of α -cleavage and subsequent coupling, disproportionation and hydrogen abstraction processes depend on the structure of the ketones and stability of the radical fragments that are ejected.

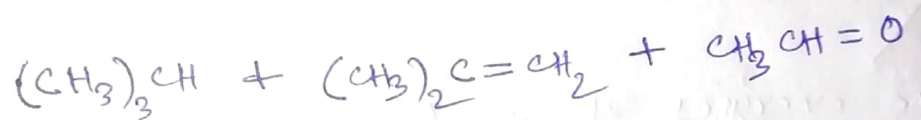
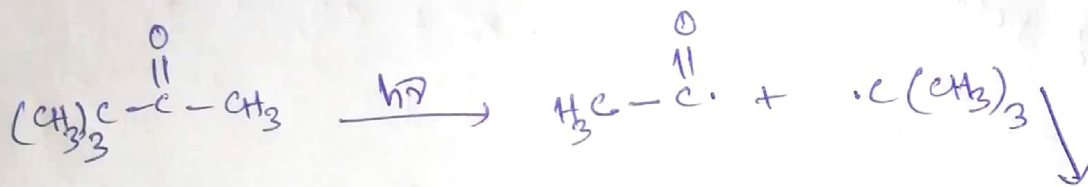
e.g. \longrightarrow

① Dibenzyl ketone undergoes photochemical α -cleavage.

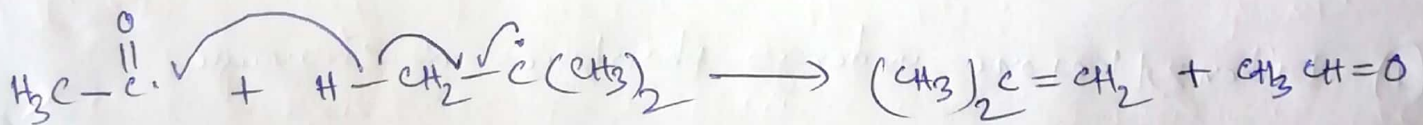
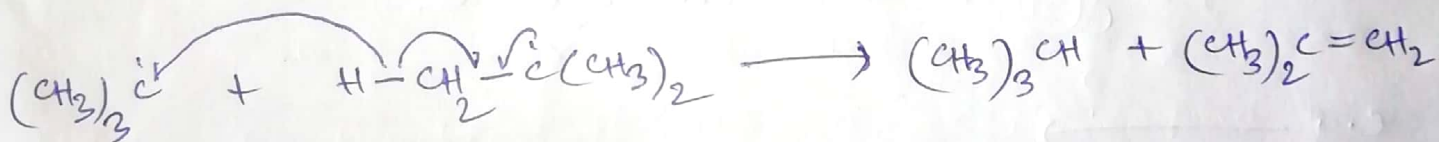




② In Unsymmetrical ketones, α -cleavage preferably takes place at the site of alkyl group that can form relatively more stable free radical.



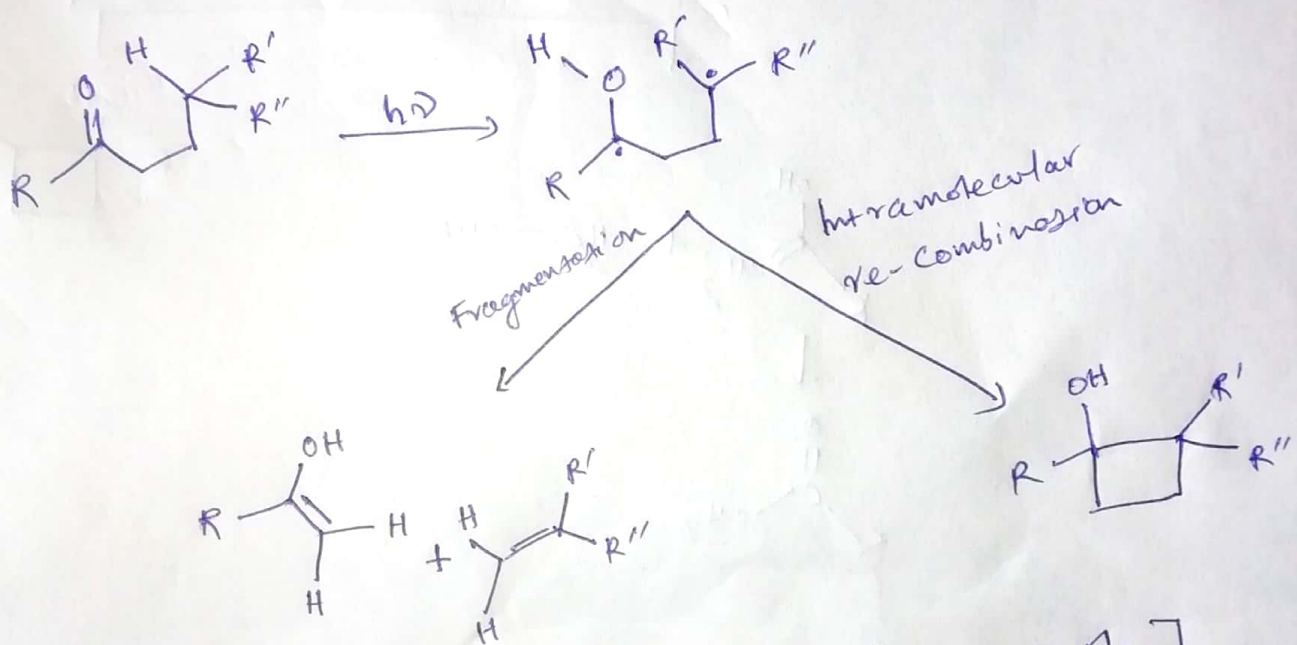
The formation of the products can be explained as follows -



Norish type II

(Intra-molecular and γ -hydrogen)

Aliphatic and Aromatic ketones having propyl or larger alkyl group as a carbonyl substituent on photoirradiation undergo intra-molecular hydrogen abstraction preferably from γ -carbon to give diradicals, which on β -cleavage or ring closure give ketone and cyclobutanol derivatives. The β -cleavage results in the formation of an alkene and a new carbonyl compound.

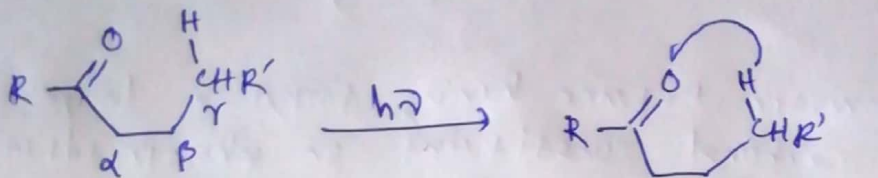


[wikipedia example]

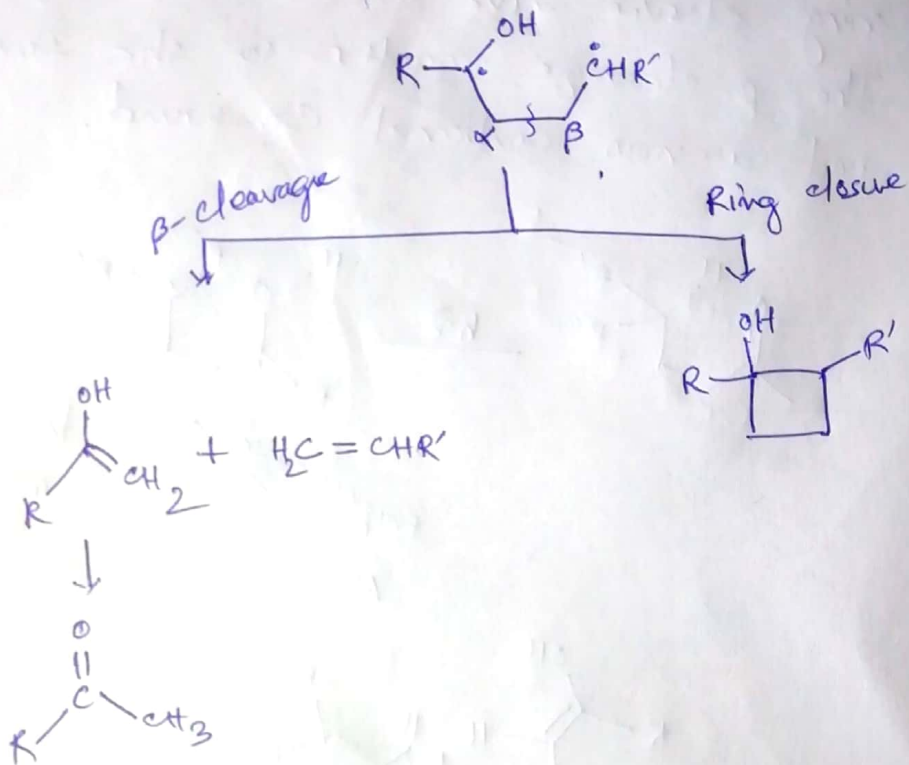
All these reactions processes are collectively known as Norish type-II cleavage reactions.

eg →

①



R, R' = Alkyl, aryl



②

