

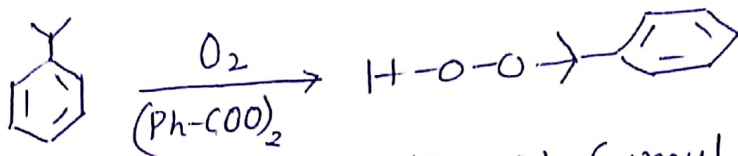
# Paper-cc VIII (Organic chemistry II)

## Free radical Reaction

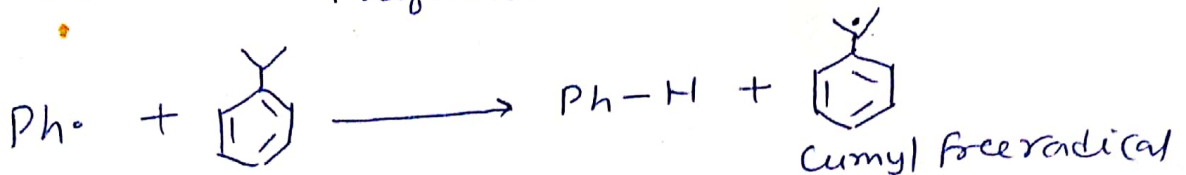
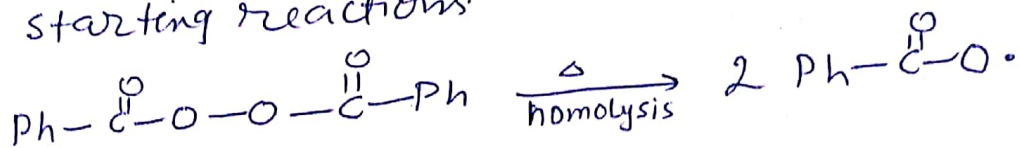
Autooxidation — Reactions of compounds with oxygen with the developments of flames are called combustions.

The flameless reaction of organic compounds with oxygen are referred to as autooxidations. In such reactions sufficiently stable radical intermediates can deliver pure compounds as major content. The free radical substitution reaction of H-atoms that are bound to tertiary carbon, allylic or benzylic carbon atoms.

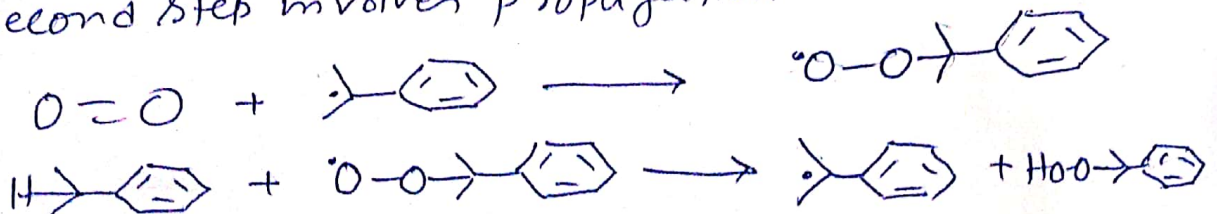
e.g. The industrial synthesis of Cumene hydroperoxide from Cumene and air is accompanied by autooxidation. Oxidation of Cumene is initiated by catalytic amount of di-tert-butyl peroxide as radical initiator.



— It involves formation of cumyl free radical as initiating radical from sequence of three starting reactions:



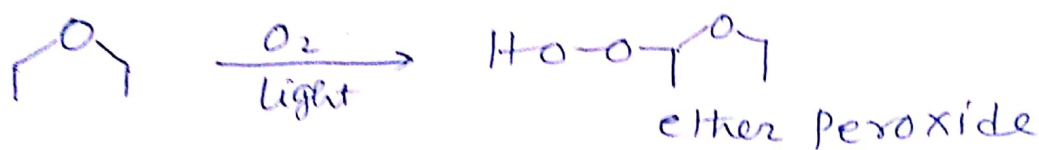
— Second step involves propagation



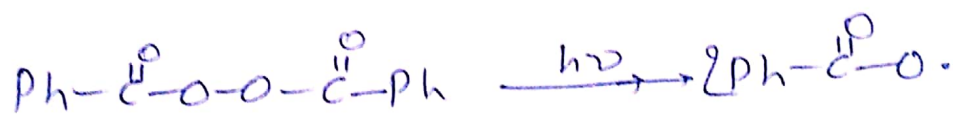
## Auto-oxidation of diethyl ether and THF

The formation of hydroperoxide of diethyl ether or THF takes place via substitution reaction in the  $\alpha$ -position to the oxygen atom.

Such peroxide formation is favoured by the formation of  $\alpha$ -oxygenated radicals which are stabilized by the free radical electron pair on the heteroatom.



— initiation step involves formation of radical from radical initiator



— Propagation step involves formation of peroxide by auto-oxidation

