

# Organic Chemistry

## Aromatic Rearrangements

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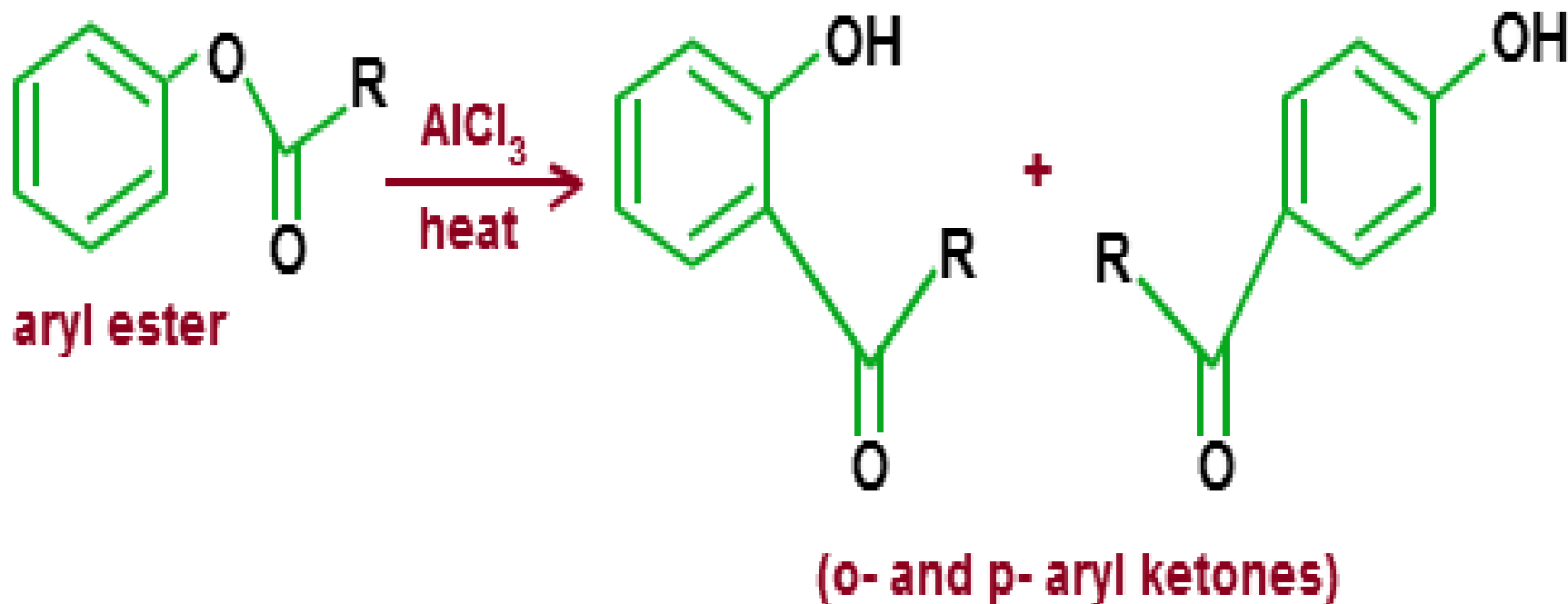
**Dr. H.N Sinha College Of Arts Commerce And Science Patur**

**Selective Organic Name Reaction**

**Msc Ist & IInd**

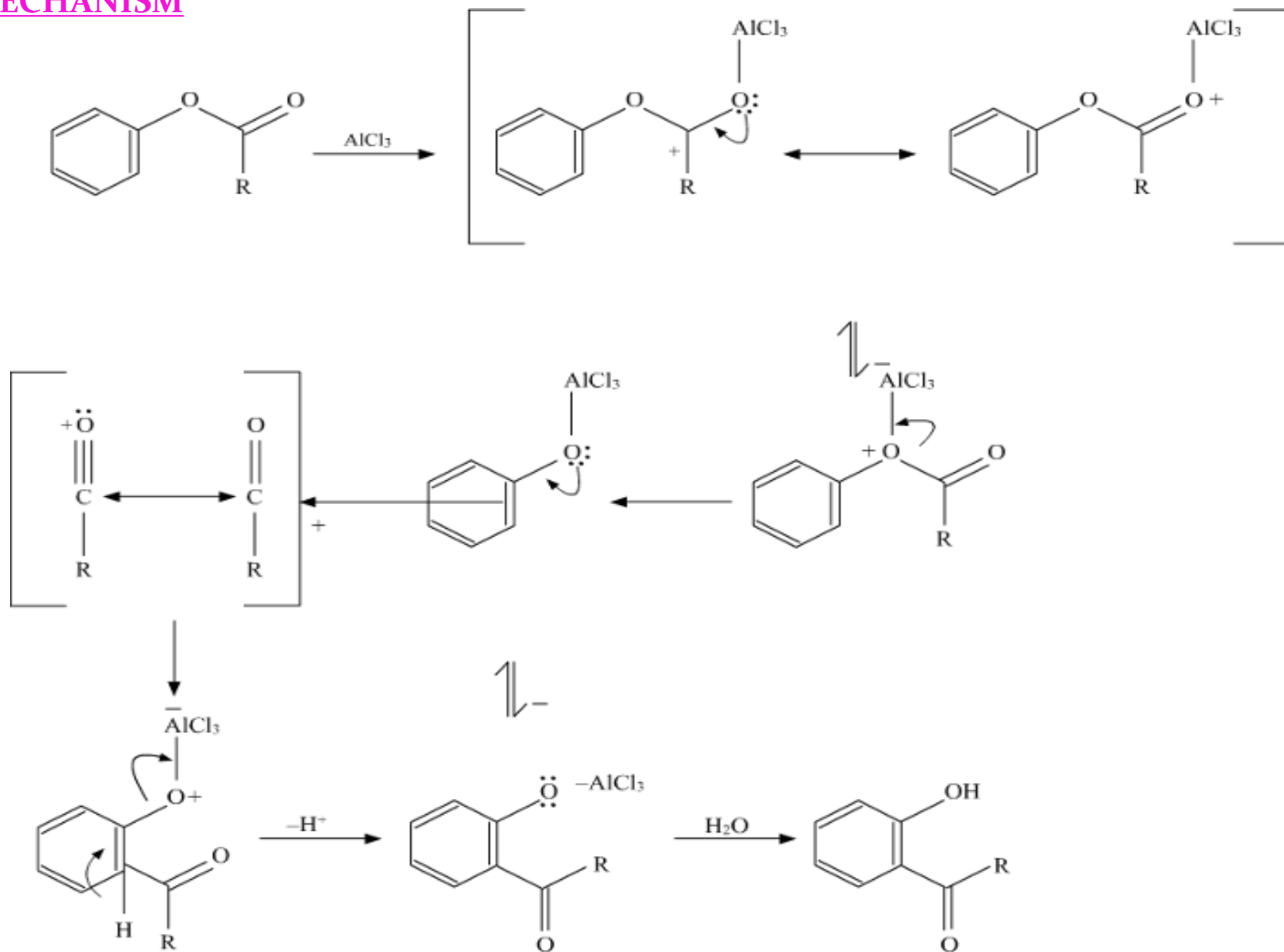
# **FRIES REARRANGEMENT**

- 1. Intra molecular Friedal –Craft Acylation**
- 2. Rearrangement of phenolic ester by heating it with Friedal –Craft catalyst.**
- 3. The reaction is catalyzed by Brønsted or Lewis acids such as HF,  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{TiCl}_4$  or  $\text{SnCl}_4$ . The acids are used in excess of the stoichiometric amount, especially the Lewis acids, since they form complexes with both the starting materials and products.**



The conversion of **phenolic esters** to the corresponding **ortho and/or para substituted phenolic ketones and aldehydes**, in the presence of Lewis or Brönsted acids is called the **Fries rearrangement**.

# MECHANISM



**The Fries rearrangement has the following general features:**

- 1. usually it is carried out by heating the phenolic ester to high temperatures (80-180 °C) in the presence of at least one equivalent of Lewis acid or Brönsted acid (e.g., HF, HClO<sub>4</sub>)**
- 2. Lewis acids that catalyze the Friedel-Crafts acylation are all active but recently solid acid catalysts (e.g., zeolites, mesoporous molecular sieves) and metal triflates have also been used**
- 3. The rearrangement is general for a wide range of structural variation in both the acid and phenol component of phenolic Esters**
- 4. yields are the highest when there are electron-donating substituents on the phenol, while electronwithdrawing substituents result in very low yields or no reaction;**

**5. with polyalkylated phenols alkyl migration is often observed under the reaction conditions**

**6. the selectivity of the rearrangement to give ortho or para- substituted products largely depends on the reaction conditions (temperature, type, and amount of catalyst, solvent polarity, etc.)**

**7. at high temperatures without any solvent the ortho-acylated product dominates (TEMP > 370 °C while low temperatures favor the formation of the para-acylated product**

**8. with increasing solvent polarity the ratio of the para-acylated product increases.**

**There are two main variants of the Fries rearrangement:**

**A. Upon irradiation with light phenolic esters undergo the same transformation, which is known as the **photo-Fries rearrangement**.**

**B. An **anionic ortho-Fries rearrangement** takes place when ortho-lithiated O-aryl carbamates undergo a facile intramolecular [1,3]-acyl migration to give substituted salicylamides at room temperature.**

# **PHOTO-FRIES REARRANGEMENT**

1. The photo-initiated rearrangement of phenyl or aryl esters is generally known as the photo-Fries rearrangement or photo-Fries reaction and usually carried out in an aprotic solvent.

2. The mechanistic features of this rearrangement can be compared with the normal Fries rearrangement catalyzed by Lewis acid.

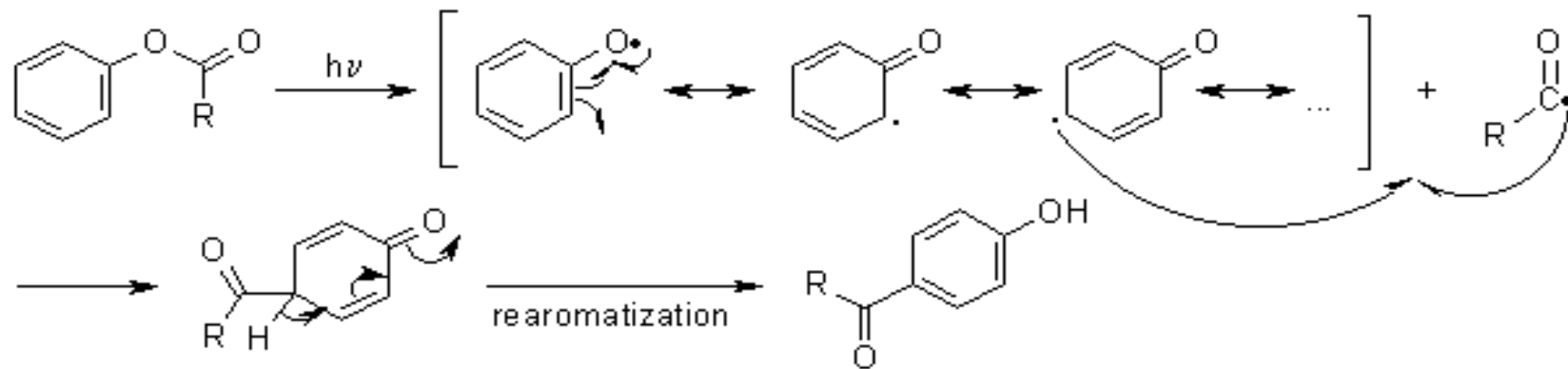
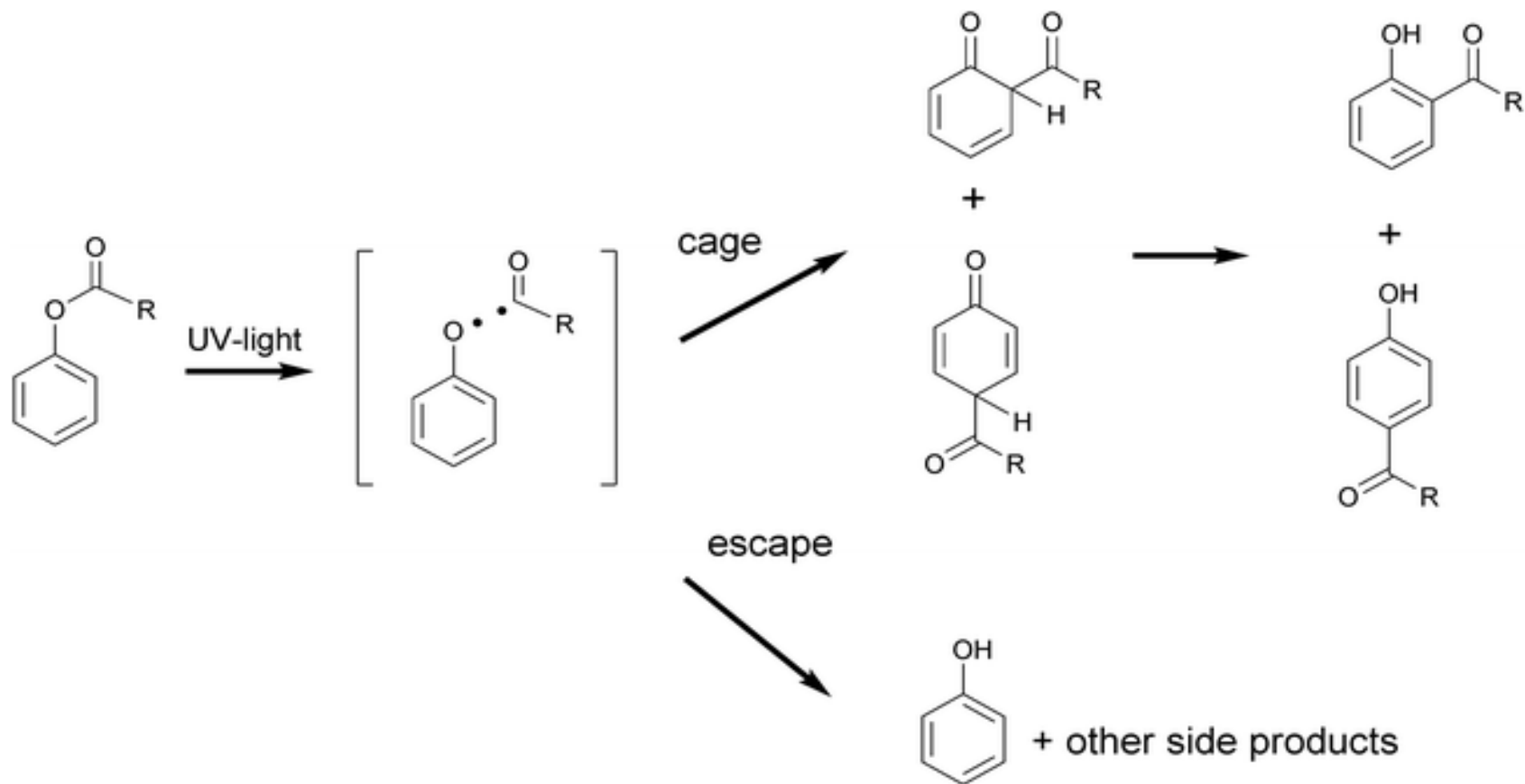
3. The study finds that regioselectivity can be further enhanced when the photo-Fries rearrangement is carried out in presence of zeolite. Besides phenyl and aryl esters, several other kinds of compounds can also undergo the hemolytic cleavage from photo-irradiation.

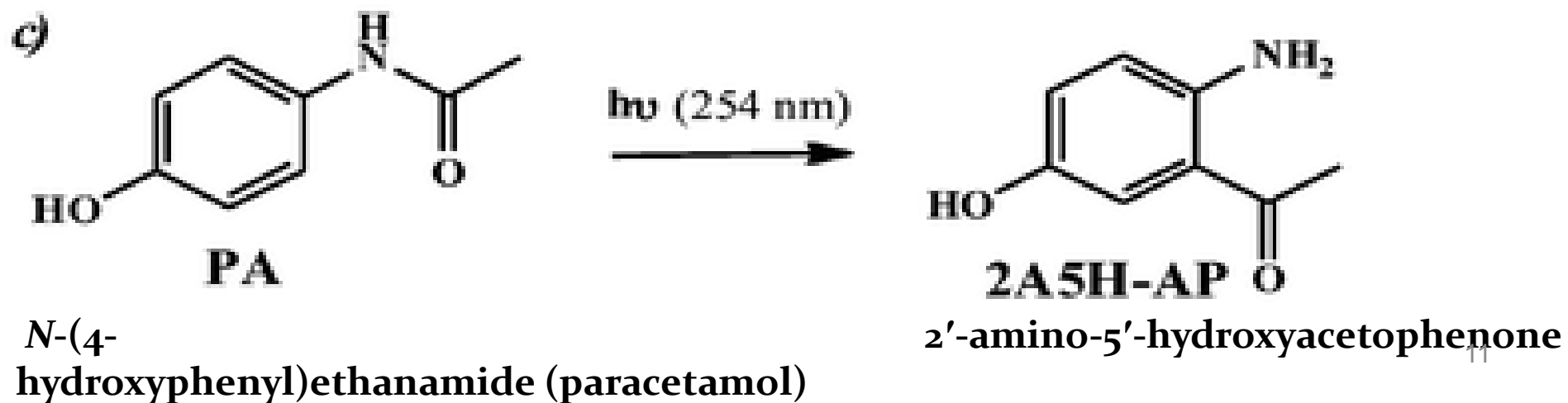
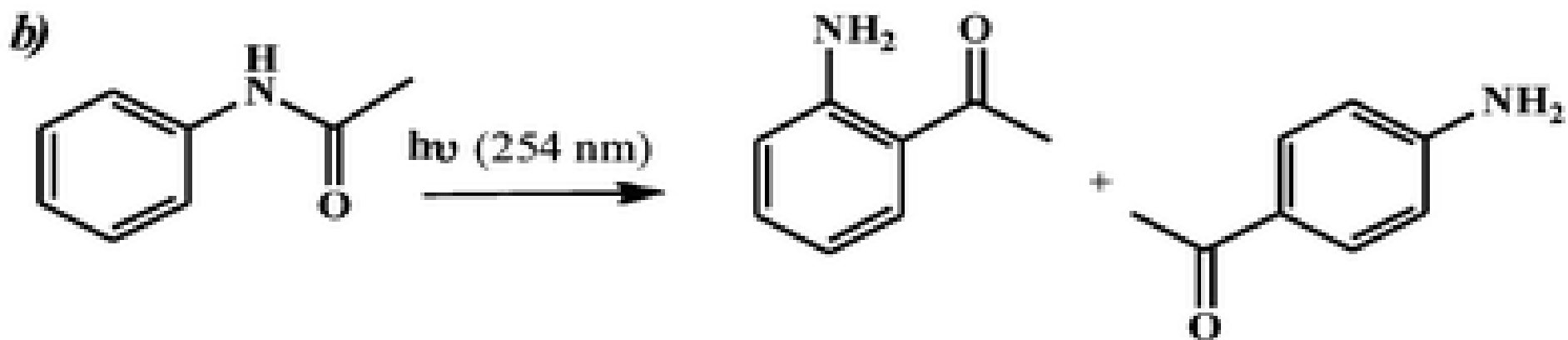
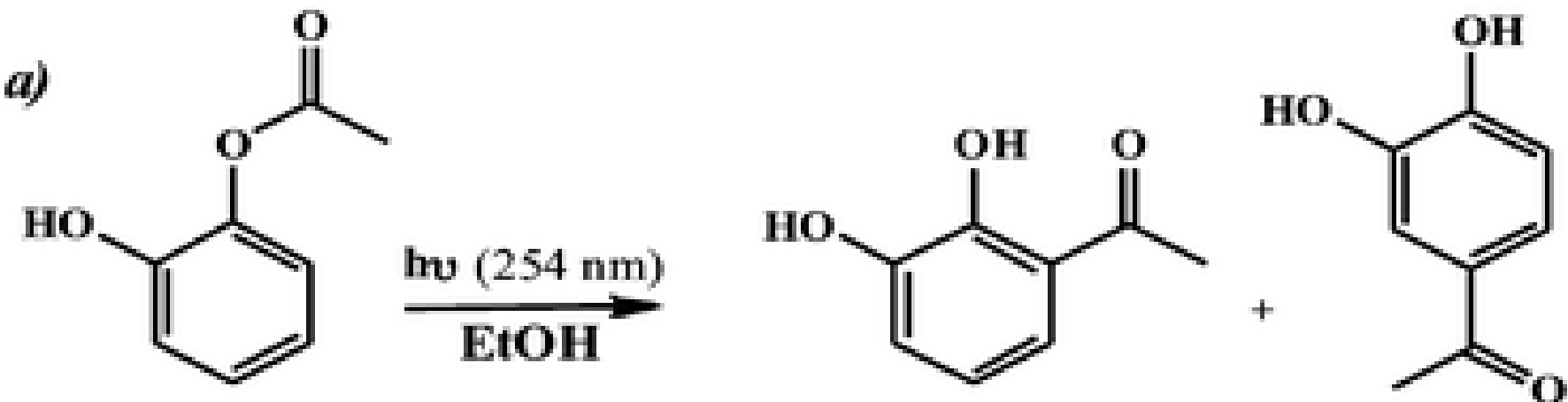


**4. This reaction is not useful in actual organic synthesis because of its different by-products.**

**5. In the normal course of reaction when the reaction is irradiated under nitrogen atmosphere with UV light, the acyl group migrates from phenolic oxygen to the C atom at o- and p-positions to form o- and p- substituted products.**

**6. Its predominantly an intra molecular free radical process hence both the o- and p- products are obtained.**





THANK  
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