Asian Journal of Chemistry Vol. 5, No. 4 (1993), 831–835

Photo-Fries Rearrangement of 1-Naphthyl Acetate and 2-Naphthyl Acetate (Photochemical Transformation)†

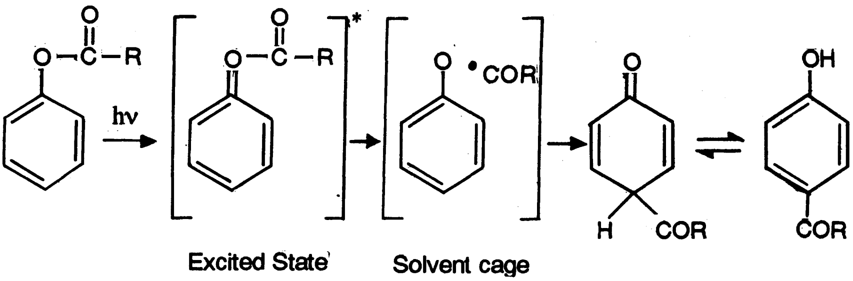
R.P.S. CHAUHAN*, M.P. SINGH, V.K. DUBEY** and UTTAM BAHADUR SINGH
P.G. Department of Chemistry
Gaya College (Magadh University) Gaya-823001, India

Photo-fries rearrangement of 1-naphthyl acetate and 2-naphthyl acetate gave 2-acetyl-1-naphthol and 1-acetyl-2-naphthol respectively. The progress of reactions and identification of compounds were confirmed by TLC, NMR and IR spectra.

INTRODUCTION

Phenolic esters are rearranged by heating with Friedel Crafts catalysts as a synthetically useful reaction known as Fries rearrangement. This rearrangement can also be carried out with UV light in place of catalyst and is called photo-fries rearrangement. In other words the well known fries reaction has its photo-chemical analogue also. In the normal course of reaction when ester is irradiated under nitrogen atmosphere with UV light acyl group migrated from the phenolic oxygen to the carbon atom at o^- or p^- position giving o^- and p^- substituted products. It is predominantly an intra molecular free radical process and hence both the *ortho* and *para* migrated products are obtained.

In the present work, we have described the photo-fries rearrangement of the esters of 1-naphthol and 2-naphthol. The available evidences suggested the following mechanism for the photo-fries rearrangement.



---

†The work was completed at Delhi University, Delhi India during Dec. 23, 1991 to Jan. 11, 1992, under Refresher Course, CH–18. organised by C.P.D.H.E.

**Chemistry Department, S.G.S. Government P.G.College Sidhi (M.P.)-486 661 (India).

Formation of phenol, ArOH is always a side product, resulting from some ArO^- species that leaves the solvent-cage and abstracts a hydrogen atom from neighbouring molecule. When the reaction is performed with phenyl acetate in the gas phase (absence of solvent molecule to form a cage). Phenol was the chief product and virtually no o^- or p^--hydroxy acetophenone was formed. When this reaction was performed in methanol (as solvent) for 6 hrs., o^--hydroxy-acetophenone was the main product. 1-Naphthyl ester and 2-naphthyl ester gave 2-acetyl-1-naphthol and 1-acetyl-2-naphthol respectively in the presence of UV light.

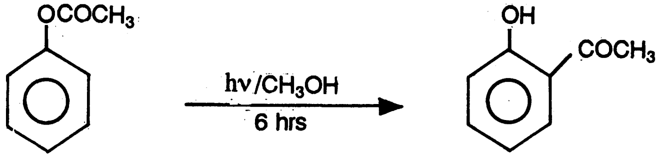
RESULTS AND DISCUSSION

Advantages of photo-fries migration over fries migration

In case of the diesters and triesters, only one of the acyl group migrats to the o^- or p^- -position. Thus photo-fries migration give very specific products which are otherwise difficult to get from fries migration.

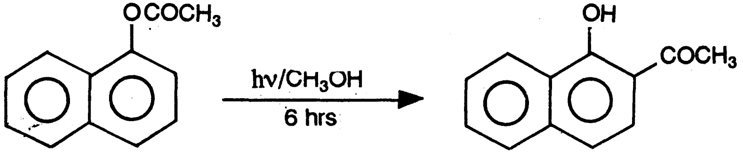
Phenyl acetate was dissolved in methanol and irradiated with PQ 125 photo physics lamp after deoxygenation with N_2 gas. After the removal of solvent the product was identified as 2-acetyl phenol. Similarly, α-naphthyl acetate and

(i)



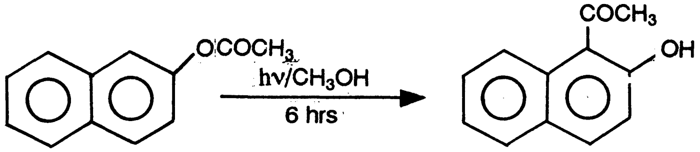
2-acetyl-phenol.

(ii)



2-acetyl-1-naphthol.

(iii)



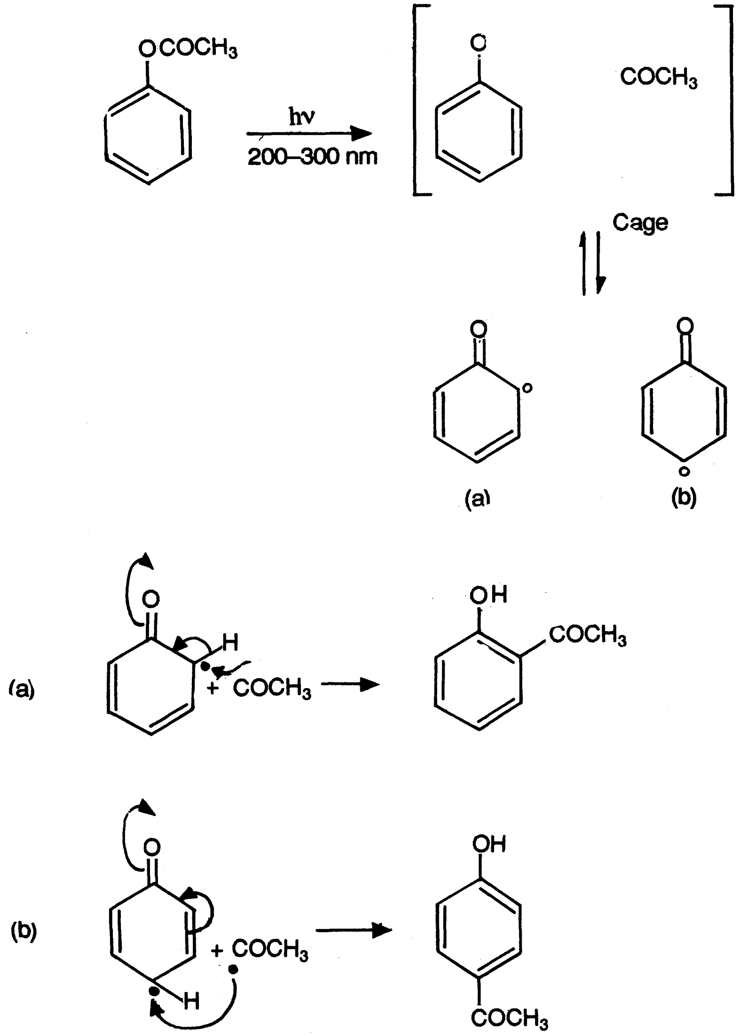
1-acetyl-2-naphthol.

β-naphthyl acetate on photolysis gave β-acetyl-α-naphthol and α-acetyl- β-naphthol respectively. In all these cases the acetyl group migrates over a double bond.

Photo-fries rearrangement 1-6 is a valuable method for the introduction of an acetyl side chain into *ortho* and *para* position to a phenolic group. It was observed by Khanna and coworkers[6] that in case of diacetoxy or triacetoxy naphthalene derivatives only one acetyl group migrated to the adjacent *ortho* position over a double bond, while the other acetoxy group(s) remained intact.

All previous studies on photo-fries migration in benzene derivatives were carried out mainly with compounds in which only one acetyl or benzoyl group was available for migration.

Mechanism (General)



EXPERIMENTAL

Preparation of 1-Naphthyl acetate

Dissolved 2 gm of α-naphthol in 5 ml of 3M NaOH sulution and 5 ml of acetic anhydride. Further added 10–20 gm of crushed ice and then shake the mixture vigourously for 10–15 minutes. The acetate of α-naphthol separated out was filtered and dried (1.4 gm) (m. pt. 49°C).

Preparation of 2-Naphthyl acetate

Dissolved 2 gm of β-naphthol in 5 ml of 3 M NaOH solution and 5 ml acetic anhydride was added, followed by 10-20 gm of crushed ice, shake the mixture vigourously for 10–15 minutes. The acetate of β-naphthol separated out was filtered and dried (1.6 gm) (m.pt 72°C).

Preparation of 2-Acetyl-1-Naphthol

In a round bottom flask, a mixture of 1-naphthyl acetate (1 mol) and anhydrous $AlCl_3$ (3.3 mol) was heated on a water bath at 100°C for 2 hrs. The reaction mixture was dissolved in ice cold water and the product steam distilled. m. pt. 100°C.

Preparation of 1-Acetyl-2-Naphthol

In a 100 ml round bottom flask, 2-naphthyl acetate (2 gm) anhydrous $AlCl_3$ (3 gm) and nitrobenzene (5 ml) were heated on a water bath at 100°C for 2 hrs. The reaction mixture was cooled and dissolved in water. Steam distillation of the mixture gave the product 1-acetyl-2-naphthol (2.6 gm) (m.pt. 107°C).

(v) Photo-fries Rearrangement of 1-Naphthylacetate

Reactant, 1-naphthyl acetate 0.4 gm was dissolved in 75 ml methanol. The solution was irradiated under nitrogen atmosphere at low wave length (200–380 mm) using a 125 W photophysics UV lamp for 6 hrs. After the removal of methanol the product was separated by column chromatography using silica gel. The product 2-acetyl-1-naphthol was confirmed by NMR and IR spectroscopy.

NMR (Nujol) δ14.0, δ2.6, H–8– δ8.4, δ7.1–7.65.

IR Supported the presence of carbonyl group in the compound.

Photo-fries-Rearrangement of 2-Naphthylacetate

Reactants 2-naphthyl acetate 0.4 gm was dissolved in 75 ml methanol. The solution was irradiated under nitrogen atmosphere at low wave length (200–380 nm) using a 125 W photo-physics UV lamp for 6 hrs. The progress of the reaction was monitored on TLC. The product was isolated by column chromatography using as an adsorbent and pure benzene as solvent. The product was identified as 1-acetyl-2-naphthol by m m.p., NMR and IR spectra.

NMR. δ2.7, H–1, H–5, δ7.2 and 8.2, δ7.5–7.8 (H7,8,4,3)

IR supported the presence of acetyl group in the compound.

ACKNOWLEDGEMENT

The authors are thankful to Prof R.N. Khanna, of Delhi University, Delhi for his valuable and fruitful suggestions. We are also grateful to Dr. P.K. Singh and Miss Joytsna Sharma for day to day guidance and help given to us. Thanks are due to Prof. G.B.V. Subramaniam and Dr. Sangeeta Pandeta for all round guidance and help.

REFERENCES

1. J.C. Anderson and C.B. Reese, *Proc. Chem. Soc.*, 217 (1960).
2. V.P. Pathak, T.R. Saini and R.N. Khanna, *Manatsch. Chem.*, **114**, 1269 (1983).
3. V.P. Pathak and R.N. Khanna, *Synthesis*, **11**, 882 (1981).
4. D.S. Bells, K. Chaffner and Hoigne, *Helv. Chem. Acta.*, **57**, 1980 (1968).
5. Y. Ohto, M. Shizuka, S. Kekiguchi and K. Matsui, *Bull. Chem. Soc. (Jap)*, **47**, 1209 (1974).
6. P.K. Sharma and R.N. Khanna, *Indian J. Chem.*, **23B**, 891 (1984).

(*Received*: 1 March 1992; *Accepted*: 1 February 1993) AJC–538