Tetrahedron Letters No. 14, pp. 873-875, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE PHOTOCHEMICAL REARRANGEMENT OF N-ACYLANILINES[1]

Dov Elad
Daniel Sieff Research Institute, The Weizmann Institute
of Science, Rehovoth, Israel

(Received 2 March 1963)

THE rearrangement of N-acylanilines to amino ketones at elevated temperatures in the presence of aluminum chloride has been known for some time.[2] We would like to report that the photolysis of aryl amides of aliphatic acids at room temperature involves a similar migration of the acyl group from the side-chain nitrogen to the aromatic nucleus. The photochemical rearrangement of aryl esters, i.e. the Fries rearrangement, has been reported recently.[3]

Irradiation[4] of acetanilide (3g.) in absolute ethanol (100ml.) for 8 hours gave o-aminoacetophenone (20%), p-aminoacetophenone(25%) and aniline (18%).

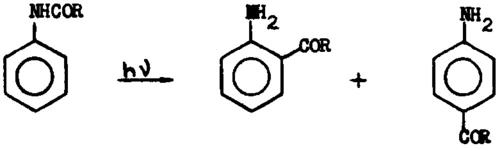
---

[1] Photochemical Studies. Part IV. For Part III see D. Elad, Tetrahedron Letters in press.

[2] (a) D.N. Kursanov, Zh. Obshch. Khim. (J. Gen. Chem. U.S.S.R.) 13, 286 (1943); Chem. Abstr. 38, 959 (1944). (b) J.F.J. Dippy and J.H. Wood, J. Chem. Soc. 2719 (1949); Nature 157, 408 (1946).

[3] J.C. Anderson and C.B. Reese, Proc. Chem. Soc. 217 (1960); H. Kobsa, J. Org. Chem. 27, 2293 (1962).

[4] Hanau Q81 high pressure mercury vapour lamps fitted into quartz immersion tubes.



$R = CH_3, C_2H_5$ or $n\text{-}C_3H_7$

Similarly, irradiation of an alcoholic solution of propionanilide gave o-aminopropiophenone (22%), p-aminopropiophenone (25%) and aniline (20%), while butyranilide gave o-aminobutyrophenone (18%), p-aminobutyrophenone (23%) and aniline (21%). The solid amino ketones were identified by their melting points, mixed melting points and infrared spectra which were identical with those of authentic samples. The liquid products were identified by their retention times in gas-liquid chromatography and further by their N-benzoyl derivatives which were identical with authentic specimens.

The aluminum chloride-induced rearrangement of N-acylanilines is reported to be intermolecular and to yield the para amino ketones,[2,5] whereas the photochemical rearrangement produces appreciable amounts of the ortho isomers. We found that both ortho and para isomers were stable under our reaction conditions and therefore neither is an intermediate in the formation of the other.

The mechanism of the photochemical rearrangement has not yet been established. Preliminary experiments showed that irradiation of an alcoholic solution of acetanilide containing o-toluidine produced mainly o-aminoacetophenone and p-aminoacetophenone together with some 2-amino-

---

[5] J.F.J. Dippy and J.H. Wood[2b] detected the formation of some o-aminoacetophenone in the case of acetanilide.

3-methylacetophenone and 4-amino-3-methylacetophenone, which were detected by gas-liquid chromatography. Similarly, photolysis of o-acetotoluidide in the presence of aniline gave mainly 2-amino-3-methylacetophenone and 4-amino-3-methylacetophenone together with some o-aminoacetophenone and p-aminoacetophenone.

Further studies of the rearrangement and the mechanism are in progress.

Acknowledgement - We are indebted to Prof. F. Sondheimer for his interest and to Mr. M. Kaczynski for the preparation of the authentic amino ketones.