

\$0040-4039(96)00242-0

Studies on Enamides. Part-5¹: A Novel Pathway for Photochemical Reaction of N-1-Cyclohexenyl-N-Phenylarylamides

Somnath Ghosh*, Bidisha Nandi and Yasmin Saima (in part)
Department of Chemistry, Jadavpur University, Calcutta 700032, India

Abstract: The oxidative photolysis of N-1-cyclohexenyl-N-phenylarylamides has culminated in a photochemical synthesis of anilides by a novel reaction pathway. Copyright © 1996 Elsevier Science Ltd

The photochemical reaction of enamides, as well documented in the literature², involves two major pathways - photochemical rearrangements and photocyclisations and these have been extensively utilised for the synthesis of complex heterocycles, alkaloids and aza-steroids. But there is no example known till date where the vinylic nitrogen bond of an enamide has undergone fission during photolysis. In the present communication, we wish to report for the first time an unexpected cleavage of the vinylic nitrogen bond of the title enamides 1(a-d) while attempting to synthesise the hexahydrophenanthridones 3 by the oxidative irradiation of 1.

Irradiation³ of a methanolic solution (350 ml) of 1a(3.61 mmol) in the presence of equimolar amount of iodine as oxidant (Scheme-1) under nitrogen atmosphere for 8 hr. neatly afforded, after usual workup and chromatography over silica gel, to our utter surprise benzanilide (2a) (52%), instead of the expected 3. That the formation of benzanilide was not an artifact of the reaction was shown by the successive photolysis of 1(b-d) - all of which gave the anilides in varying yields (Table). Although we could synthesise 3 under non-oxidative condition, such photochemical synthesis of anilides is unknown, though not intended. However, it unravels a new reaction pathway for enamide photolysis under oxidative condition in the presence of an electron-withdrawing group (EWG), i.e., phenyl on the nitrogen atom of the enamide 1.

SCHEME - 1

R3

R2

R1

$$\frac{R_3}{R_1}$$
 $\frac{hv \ / \ MeOH}{I_2}$

R1

 $\frac{hv \ / \ MeOH}{I_2}$

R2

 $\frac{R_1}{R_1}$
 $\frac{hv \ / \ MeOH}{I_2}$

R2

 $\frac{R_1}{R_1}$
 $\frac{R_2}{R_1}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_1}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_1}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_2}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_3}$
 $\frac{R_2}{R_1}$
 $\frac{R_2}{R_2}$
 $\frac{R_1}{R_2}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_1}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_3}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_3}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_3}{R_3}$
 $\frac{R_2}{R_3}$
 $\frac{R_3}{R_3}$
 $\frac{R_3}{R_3}$

We, therefore, became interested to study the mechanism of this reaction and reasoned that the reaction probably involved an iodine radical induced isomerisation of the double bond of the cyclohexene ring of 1, followed by a fission of C-N bond to afford the anilides 2. In order to establish this, we carried out the irradiation of 1a in the presence of N-bromosuccinimide in methanol (Scheme-2), whence we could isolate 2a in 53% yield. The reaction, therefore, proceeded through an allylic bromination and this was further substantiated by the fact that the bromo-enamide 5, mp. 94-95° (diethyl ether - petroleum ether, 40-60°), IR(Nujol) v max 1640 cm⁻¹, ¹H NMR (CDCl₃) 8 5.48 (1H, dd, J=6.0, 2.0 Hz)

Substrate (1)	Time in hr.	Yield (%) of Anilide (2)	IR (Nujol) v _{max} cm ⁻¹
a: 3.61 mmol	8	52	3350, 1660
b : 3.26 mmol	14.5	68	3335, 1645
c: 2.97 mmol	20	83	3310, 1640
d : 3.11 mmol	18	43	3250 , 1660

SCHEME - 2

SCHEME - 3

Ar
$$hv$$
 $I_2 \text{ or NBS}$
 $(-HX)$
 $X = Br, I$

Ar
 Ar
 Ar
 C_6H_5
 C_6H_5

on irradiation in methanol for 3 hr. yielded 73% of 2a, showing it to be a true intermediate in the reaction profile (Scheme - 3).

The synthesis of anilides was not our objective but, we became interested in the mechanism of this novel and unknown reaction pathway for oxidative enamide photolysis. We conclude that the present study shows a remarkable effect of the presence of EWG⁴ on the nitrogen atom of enamides on the course of their photochemical reactions under oxidative conditions.

Acknowledgements: The authors thank Prof. A.Chatterjee for his keen interest, Prof. S. Ghosh and Dr. S.C.Roy, IACS, Calcutta for providing computer facilities and ¹H NMR spectra and UGC, New Delhi for financial assistance (to BN).

References and Notes

- 1. Part-4: Datta, I; Das, T.K. (in part); Ghosh, S.N. Tetrahedron 1990, 46, 6821.
- Reviews: a) Sharma, R.K.; Kharasch, N. Angew. Chem. Int. Ed. Engl. 1968, 7, 36; b) Lenz, G.R. Synthesis, 1978, 489; c) Mallory, F.B.; Mallory, C.W. Org. React. 1984, 30, 1.
- Irradiation experiments were performed at room temperature using a low pressure mercury lamp (16 W, > 90% 254 nm, Applied Photophysics Ltd., England) in a quartz vessel (immersion type).
- 4. The presence of an **EWG** such as carbonyl^{2b} or a phenyl/aryl^{2b} on the nitrogen atom of enamides is known to afford rearranged products (1,3 or 1,5 -) on non-oxidative photolysis.