Tetrahedron Letters,Vol.28,No.31,pp 3613-3614,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A NOVEL PHOTOCHEMICAL 1,4-ACYL MIGRATION IN ENOL ESTERS. THE PHOTOLYSIS OF ENOL ACETATES OF 3-PHENYLPROPIOPHENONES

M. Alvaro,[a] V. Baldoví,[a] H. García,[a] M.A. Miranda[b*] and J. Primo[a]

[a] Departamento de Química, ETSII, Universidad Politécnica, Apartado 22012, 46071-Valencia, Spain. [b] Departamento de Química Orgánica, Facultad de Farmacia, Av. Blasco Ibañez 13, 46010-Valencia, Spain

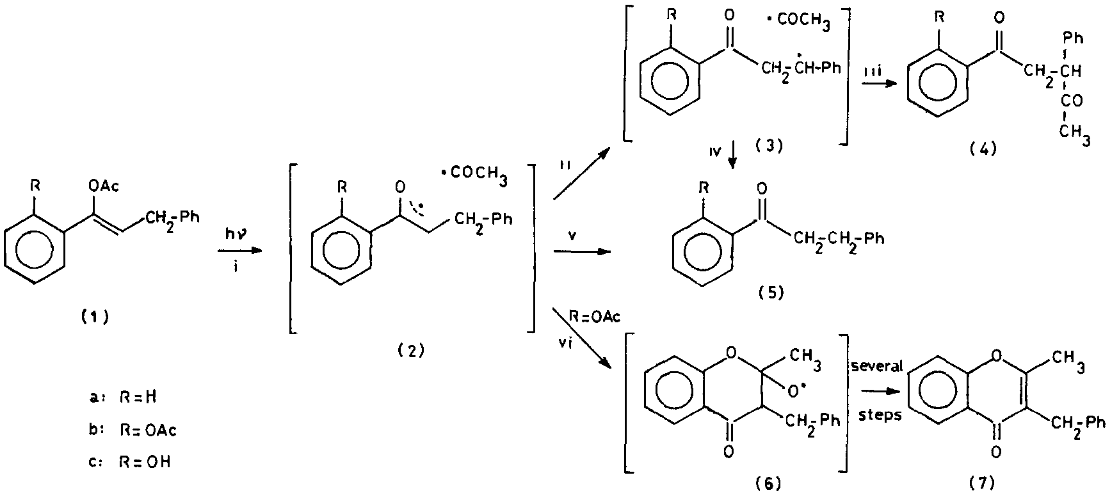
Abstract. Photolysis of the enol acetates **1a,b** gives the 1,4-diketones **4a,b** by a mechanism involving a primary homolytic carbonyl-oxygen bond cleavage, followed by 1,2-hydrogen shift and in cage recombination.

Enol esters undergo a photochemical 1,3-acyl shift, as the most general reaction, to give β-diketones.[1-2] There are also some isolated studies illustrating the ability of certain enol esters to undergo a photochemical 1,2[3] or 1,5[4] acyl shift. However, as far as we are aware, no 1,4 migration of the acyl group in enol esters has been reported as yet.

We wish to report on the irradiation of the enol acetate of 3-phenylpropiophenone **1a**,[5] whereby 3-phenylpropiophenone **5a** (34%) and 1,3-diphenyl-1,4-pentanedione **4a** (26%) were formed as the major products. A little amount of the starting material **1a** (10%) was recovered unchanged. The expected 1,3-acetyl shift product was not present in the photolysis mixture.

These results may be rationalized in terms of a primary homolytic carbonyl-oxygen bond cleavage of the enol ester moiety (process i), giving rise to the acetyl and **2a** radicals. Subsequent 1,2-hydrogen atom migration in **2a** (process ii) would lead to the benzylic radical **3a**, which could further undergo hydrogen abstraction from the medium (process iv) or recombination with the acetyl radical (process iii); however the formation of **5a** by direct hydrogen abstraction from the medium by **2a** (process v) cannot be completely ruled out.

In order to obtain data in support of our mechanistic proposal, we also performed the irradiation of the *o*-acetoxy derivative **1b**. It is known that *o*-acyloxy substitution in acetoxystyrenes[6,7] gives rise to intramolecular reactions from the resulting *o*-acyloxybenzoylmethyl radicals, yielding



products with a benzopyran ring. This could be an elegant method of trapping this type of intermediate, if it were formed during the course of the photolysis.

As a matter of fact, photolysis of **1b**[5] led to the chromone **7** (24%), together with the 1,4-pentanedione **4b** (16%) and the propiophenones **5b** (32%) and **5c** (6%). The 1,4-acyl migration product **4b** was formed in this case with a yield substantially lower than that of **4a** from **1a**, evidently due to the existence of the competitive pathway leading to the chromone **7** (process vi). Thus, the isolation of **7** constitutes an evidence for the formation of **2b** as the primary intermediate. Finally, **5b** could arise from **2b** or **3b** by hydrogen abstraction, and the little amount of **5c** could be formed from **5b** by a photochemical deacetylation similar to those observed in related o-acetoxyphenyl ketones.[7]

REFERENCES AND NOTES

1. D. Bellus, Adv. Photochem., 1971, 8, 109.
2. K.N. Houk, Chem. Rev., 1976, 76, 1.
3. D. Armesto, M.J. Ortiz, R. Pérez-Osorio and W.M Horspool, Tetrahedron Lett., 1983,24, 1197.
4. A. Yogev, M. Gorodetsky and Y. Mazur, J. Am. Chem. Soc., 1964, 86, 5213.
5. Enol acetates **1a,b** were obtained by treatment of the corresponding 3-phenylpropiophenones **5a,b** with isopropenyl acetate, in the presence of p-toluenesulphonic acid as catalyst. Irradiations (500 mg) were performed in hexane solutions (300 ml) using a quartz immersion well photoreactor provided with a medium pressure mercury lamp purging continously with nitrogen for 6 h.
6. H. García, R. Martínez-Utrilla and M.A. Miranda, Tetrahedron Lett., 1981, 22, 1749.
7. H. García, R. Martínez-Utrilla and M.A. Miranda, Liebigs Ann. Chem., 1985, 589.

(Received in UK 10 March 1987)