Tetrahedron Letters Vol. 21, pp 3925 - 3926
0040-4039/80/1001-3925$02.00/0

# THE PHOTOCHEMISTRY OF α-ACETOXYSTYRENE

Hermenegildo García[a], Roberto Martínez-Utrilla[b] and Miguel Angel Miranda[a,*]

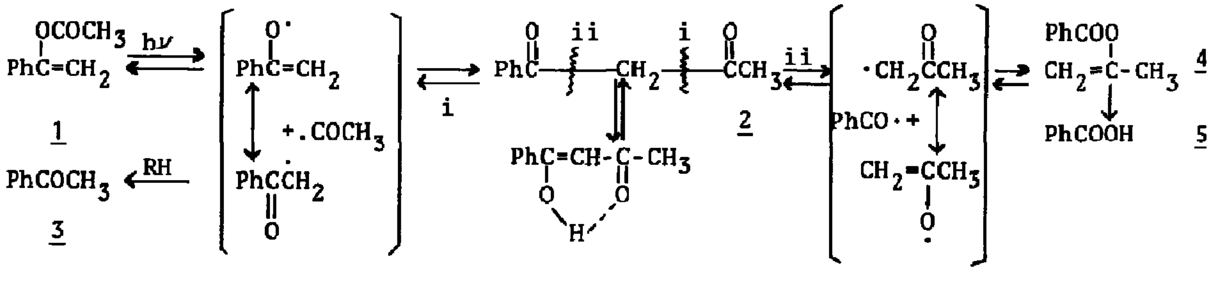
a) Departamento de Química Orgánica. Facultad de Farmacia. Universidad de Valencia.
b) Instituto de Química Orgánica General (C.S.I.C.) Madrid. Spain.

Summary: Photolysis of α-acetoxystyrene leads to isopropenyl benzoate as a result of reverse photo-Fries rearrangement of the intermediate benzoylacetone.

The photo-Fries rearrangement of aryl esters is a well established process[1] that we have recently investigated with synthetic purposes[2]. Enol esters have been also found to undergo a similar photorearrangement[3].

The present paper is concerned with the photochemical behavior of α-acetoxystyrene 1. A priori, 1,3-acetyl migration was expected to occur, followed by thermal equilibration of the resulting benzoylacetone 2 with the enol form. In fact, irradiation of 1 in hexane solution using a medium pressure mercury lamp and a conventional quartz immersion well yielded the expected product 2 (8%), which was identified by comparison with an authentic sample. In addition to the "normal" product, four other products were isolated by column chromatography of the complex reaction mixture: a considerable amount of starting material 1 (14%), acetophenone 3 (3%), isopropenyl benzoate 4 (9%) and benzoic acid 5 (13%). The photomixture contained also some unidentified polymer.

Satisfactory correlation of the data can be made by the following Scheme:



The photoexcitation results in a primary cleavage of the ester O-CO bond to give a radical pair, enclosed in a solvent cage. Vinyloxy radicals are mesomeric systems and their recombination with acyl radicals leads to a 1,3-dicarbonyl compound 2 or to the unrearranged enol ester 1. If vinyloxy radicals escape from the cage and abstract hydrogen from the solvent, acetophenone 3 is formed. Compound 2 can further react by cleavage of the C-C bond α to the acetyl (process i) or to the benzoyl group (process ii). In both cases a pair of radicals is obtained that can recombine in the solvent cage, affording α-acetoxystyrene 1 (i) or isopropenyl benzoate 4 (ii) respectively. The isolation of benzoic acid 5 can be explained by fission of the vinyl-oxygen bond of 4 upon irradiation, although formation during isolation by hydrolysis of isopropenyl benzoate is not excluded.

Our conclusions seem to be in conflict with previous work in this field. It has been reported[4] that the direct irradiation of the enolic form of 2 causes exclusively its partial tautomerization to the apparently photostable diketonic form. One way to conciliate both series of results might come from the assumption that enolization is a singlet photoprocess whereas C-C bond fission is a triplet one. If the former competes favourably with intersystem crossing in the case of enolizable β-diketones, direct irradiation would only affect the keto/enol ratio. To enhance the prospects of an α C-C bond rupture, photosensitization would be the appropriate route. To check this hypothesis, we have irradiated 2 in the presence of acetophenone -a triplet sensitizer that is also a photoproduct of 1- and using DMSO as solvent, where the initial concentration of the diketo form is comparatively high. Under these conditions, the formation of an appreciable amount of 4 has been observed.

This result renders support for our reaction Scheme. It shows that the reverse photo-Fries rearrangement of benzoylacetone -an enolizable β-diketone- is possible under photosensitization conditions. To our best knowlege this kind of reaction is without precedent and up to now photochemical interconversions between exocyclic enol lactones and nonenolizable β-diketones constitute the only example known in this sense[5]. Additional work is in progress in order to elucidate the scope of this reaction.

## REFERENCES

1. a) D. Bellǔs, Adv. Photochem. 8, 109 (1971); b) M. Pfau and M. Julliard, Bull. Soc. Chim. Fr., 785 (1977).
2. a) C. Escobar, F. Fariña, R. Martínez-Utrilla and M.C. Paredes, J. Chem. Research (S), 266 (1977) and ibid. (M), 3154 (1977); b) R. Martínez-Utrilla and M.A. Miranda, Tetrahedron Letters, 2281 (1980).
3. a) M. Gorodetsky and Y. Mazur, Tetrahedron 22, 3607 (1966); b) S.P. Pappas, J.E. Alexander, G.C. Long and R.D. Zehr, J. Org. Chem. 37, 1258 (1972); c) D. Veierov, T. Bercovici, E. Fischer, Y. Mazur and A. Yogev, Helv.Chim. Acta 58, 1240 (1975).
4. a) P. Markov and I. Petkov, Tetrahedron 33, 1013 (1977); b) D. Veierov, T. Bercovici, E. Fischer, Y. Mazur and A. Yogev, J. Am. Chem. Soc. 99, 2723 (1977).
5. a) J. Rigaudy and P. Derible, Bull. Soc. Chim. Fr., 3047, 3055 and 3061 (1965); b) H. Nozaki, Y. Yamaguti, T. Okada, R. Noyori and M. Kawanisi, Tetrahedron, 23, 3993 (1967).

(Received in UK 28 July 1980)