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PHOTOCYCLIZATION OF ENOL ACETATES OF o-ACETOXYACETOPHENONES TO CHROMONES

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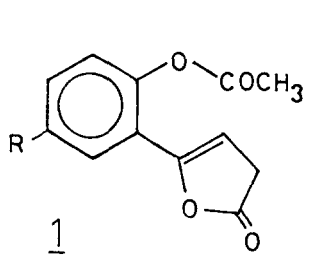
Summary: Enol acetates of o-acetoxyacetophenones give chromones upon irradiation with uv-light.

In a recent paper[1] we have reported on the formation of chromones by irradiation of o-acetoxyaryl-2(3H)-furanones 1. In order to establish whether the lactone structure is a prerequisite for cyclization, a benzene solution of the simple enol ester 2a[2] was submitted to irradiation in a quartz immersion well reactor with a medium pressure mercury lamp. Isolation of chromone 3a (20%) showed that in fact the lactone structure is not an essential requirement. Unreacted starting enol ester (30%), together with o-acetoxyacetophenone (25%), o-hydroxyacetophenone (5%) and some unidentified polymeric material accompany the chromone in the irradiated solution, justifying the poor yield of the latter compound.



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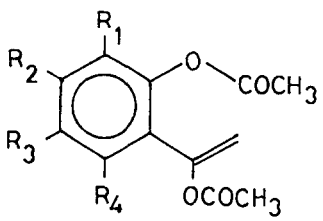
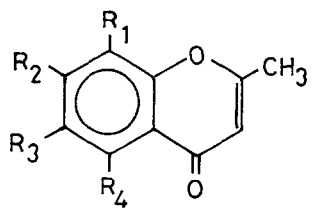


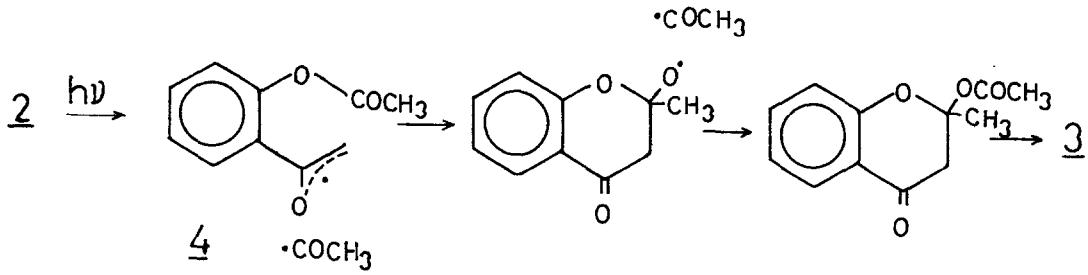
2a-g



3a-g

Other substituted enol esters 2b-g[2] afforded also the corresponding chromones 3b-g, thus confirming the general character of the reaction.

These results may be interpreted in terms of a primary cleavage of the enol acetate O-CO bond, to form the mesomeric radical 4, together with an acetyl radical. Next steps probably involve an intramolecular radical addition to the carbonyl group of the phenyl ester moiety, followed by radical recombination and acetic acid elimination.



	R_1	R_2	R_3	R_4	Yield (%)	Lit. Ref.
3a	H	H	H	H	20	3
3b	H	H	OCH_3	H	42	4
3c	H	H	Cl	H	10	5
3d	H	H	CH_3	H	15	6
3e	H	OCH_3	H	H	8	7
3f	H	OH	H	H	21	8
3g	H	CH_3	CH_3	H	16	

Many chromones and flavones are found in plants, and their synthesis under mild conditions with the concurrence of light may be of phytochemical interest. Current work is directed to optimize the chromone yields and to obtain experimental evidence in support of the proposed mechanism.

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