

Photochemical Behaviour of Furylidene Carbonyl Compounds

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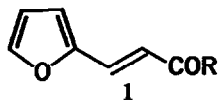
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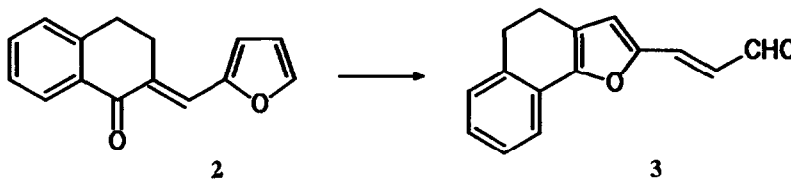
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Abstract - Photophysical and electrochemical properties of furylidene carbonyl compounds were utilized in order to explain the observed photochemical behaviour.

Cinnamic acid gives photodimers when irradiated in the solid state: this reaction is stereospecific depending on the crystal form of the starting material.¹⁻⁴ However, the reaction of the same substrate in solution does not give any dimerization products but only *cis-trans* isomerization.^{5,6} Recently we reported a new photochemical dimerization of 3-(2-furyl)acrylic derivatives **1** to give cyclobutanes.⁷ This is the first example of photochemical dimerization of arylacrylic derivatives in solution in absence of Lewis acids.^{8,9} In fact, in our experiments we used acetonitrile as solvent in the presence of benzophenone.



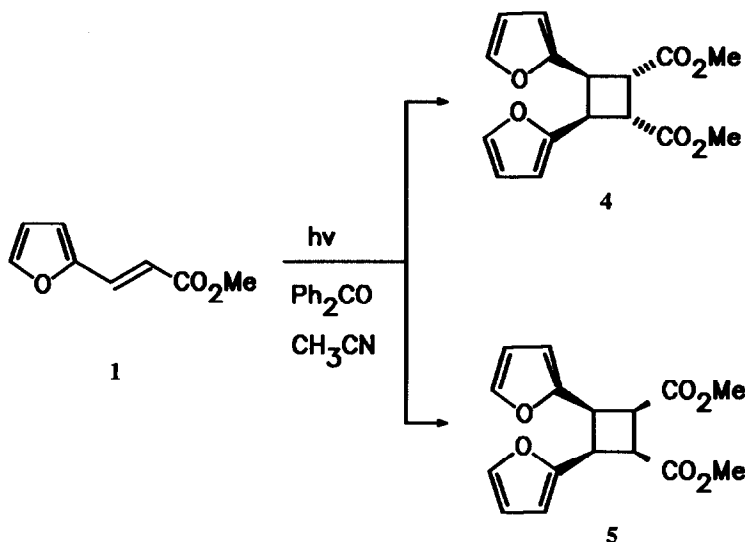
Furthermore, we have reported also that furylidenetetralones **2** do not give any dimerization product, but rather the isomerization product **3**.¹⁰



In this paper we report our results on the mechanism of these two reactions.

Results and Discussion

Irradiation of **1** in acetonitrile in the presence of benzophenone with a 500 W high pressure mercury arc in an immersion apparatus equipped with a Pyrex filter gave a mixture of **4** (61%) and **5** (27%).



Photochemical dimerization of coumarin (an arylacrylic acid derivative) in solution can be carried out using both direct and benzophenone sensitized conditions: under these different experimental conditions the reactions gave a mixture of *cis* head-to-head and *trans* head-to-head dimers.^{11,12} The different results in these reactions can be explained in terms of the involvement of different excited states. *Cis* head-to-head dimer is formed from the singlet state, while *trans* head-to-head dimer from the triplet state. Furthermore, in the latter case singlet-singlet energy transfer from coumarin to benzophenone and subsequent triplet-triplet energy transfer from benzophenone to coumarin account for the role of benzophenone in this reaction.¹³

On the basis of these reported data we decided to study the photochemical dimerization of methyl 3-(2-furyl)acrylate in order to elucidate the role of benzophenone in our experiments and the solvent effect on product distribution.

Direct irradiation of 1 in an immersion apparatus equipped with a Pyrex filter allowed us to obtain a *cis-trans* photostationary equilibrium. In different solvents (acetonitrile, methanol, ethyl acetate, ethanol, and benzene) we observed the formation of $25 \pm 1\%$ *cis*-isomer in the reaction mixture but no formation of any dimerization product. *Cis-trans* isomerization is a very fast reaction. As shown in Fig 1 the uv spectrum of 1 showed a strong absorption band at λ 299 nm ($\epsilon = 20000 \text{ M}^{-1} \text{ cm}^{-1}$). When the substrate was irradiated with a mercury lamp without filter for a few seconds, shift of the peak at $\lambda = 299$ nm to $\lambda = 302$ nm was observed. This bathochromic shift is maintained even after prolonged irradiation. Laser flash photolysis experiments showed that direct irradiation of 1 in acetonitrile, ethanol, and benzene did not produce any transient state using both 308 and 347 nm excitations. The only photoproduct obtained by uv irradiation of 1 in benzene, ethanol, and acetonitrile was the *cis* isomer (characterized by GCMS); the photoisomerization quantum yield value (0.4 in benzene at $\lambda_{\text{exc}} = 313$ nm) evidences that the *trans* \rightarrow *perp* rotation is the main decay process of the excited states of 1. Since there is no evidence of triplet state population under these experimental conditions, it strongly suggests that only the lowest singlet state is involved in the photoisomerization process.

We carried out dimerization reactions in the presence of benzophenone, the kinetic behaviour of which is shown in Fig. 2. The *cis* isomer rapidly reached $0.65 - 0.70 \times 10^{-2} \text{ M}$ concentration and maintained this concentration during all our experiments. Dimer formation followed a zero order kinetics in agreement with a sensitized reaction. We obtained $k = 1.38 \pm 0.02 \times 10^{-3} \text{ M s}^{-1}$.

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