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SINGLE ELECTRON TRANSFER INITIATED PHOTOCYCLIZATION OF SUBSTITUTED CINNAMIC ACIDS TO CORRESPONDING COUMARINS

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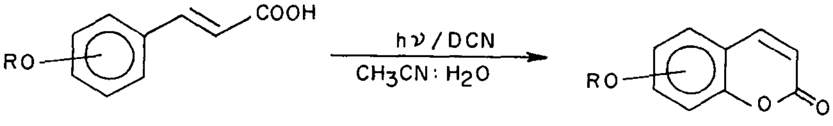
Abstract: Efficient photocyclization of substituted cinnamic acids to corresponding coumarins, initiated by single electron transfer processes, have been reported. A probable mechanism has been discussed.

Recently, exploratory and mechanistic photochemical studies have placed increasing emphasis on a new class of excited state processes that are initiated by single electron transfer (SET) from or to excited states of organic and inorganic systems[1-3]. Photosubstitution of aromatic rings have been reported, initiated by single electron transfer from the excited aryl chromophore to a suitable acceptor[4-6]. Since the key reactive intermediates in SET induced pathways are ion radicals, the nature of the chemical reactions followed in these systems could be directed on the basis of the principles applied in radical ion chemistry for target molecule synthesis. In view of the above facts, we report herein the phtocyclization of substituted cinnamic acids (bearing electron rich substituents) to give the corresponding coumarins in the presence of 1,4-dicyanonaphthalene (DCN) as electron acceptor.



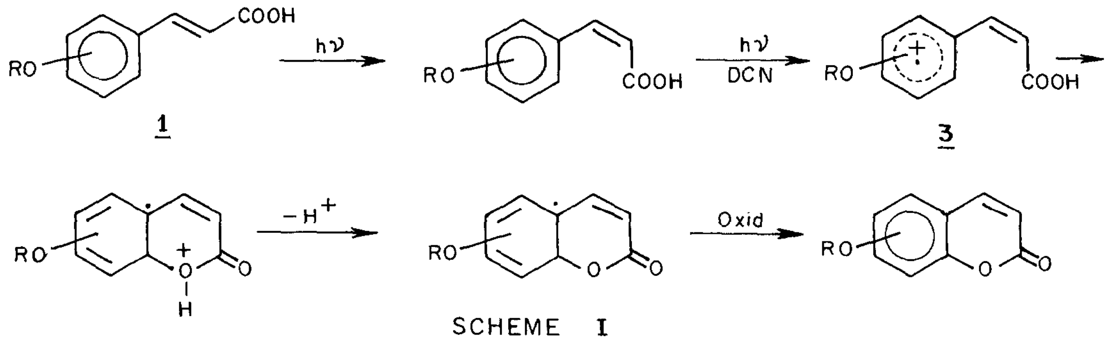
1 a–e

2

OR = a) 4-methoxy
b) 3-methoxy
c) 3,4-dimethoxy
d) 2,5-dimethoxy
e) 3,4-methylenedioxy

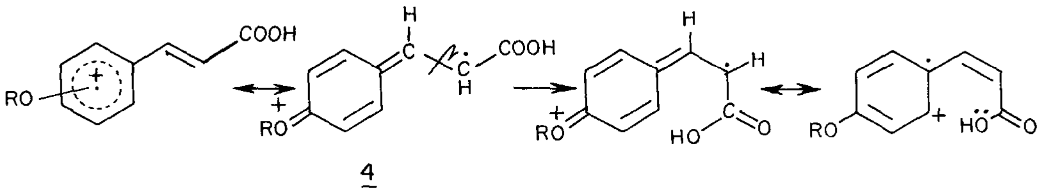
Irradiation (Pyrex filter, > 280 nm) of a solution containing substituted cinnamic acids (mainly *trans*, 5.60×10^{-3}M) and 1,4-dicyanonaphthalene (3.37×10^{-4}M) in acetonitrile : water (80:20) mixture saturated with oxygen using 125 W mercury lamp for 4-6 hr gave (conversion ≈80%) the corresponding coumarins as a single photoproduct in 60-80% yield. Reaction was found to be slow in the presence of nitrogen[4]. The coumarins were characerized by mp., ^{1}H NMR and mass spectrometry.

The photoreaction is apparently initiated by single electron transfer from the excited singlet state of electron rich aromatic ring of cinnamic acid to DCN (aryl fluoroscence is quenched by DCN with diffusion controlled rate) which generates radical cation centre in aromatic ring. Intramolecular nucleophilic attack of -OH group of carboxylic acid on the aromatic cation followed by subsequent steps as shown in Scheme I, results in the coumarin molecule. Cinnamic acid itself fails to give cyclized product under these circumstances.



SCHEME I

Intramolecular cyclization would take place only when 1 acquires *cis*-configuration. There could be two pathways for the formation of *cis*-isomer, first direct photoisomerisation of *trans*-cinnamic acid to *cis*-isomer which undergoes cyclization via electron transfer processes as shown in Scheme I.



SCHEME II

Second, the radical cation intermediate (3) could attain the *cisoid*-configuration (5) via a resonance stabilised quinonoid intermediate (4) as shown in Scheme II. Since 3-methoxycinnamic acid, where quinonoid intermediate (4) is not possible, also underwent cyclization to give 8-methoxycoumarin, this rules out the mechanism outlined in Scheme II. This observation also finds support from the work of McKillop et al,[7] where a quinonoid intermediate of type (4) produced by the reaction of 4-alkoxycinnamic acid with thallium(III) trifluoroacetate has been shown to give a novel dimerised product 2,6-diaryl-3,7-dioxobicyclo[3,3,O]octane 4,8-dione instead of coumarins. Therefore, it could be suggested that cyclization of 1 is taking place by the mechanism as proposed in Scheme I. The detiled mechanistic and photophysical aspects of this reaction would be published elsewhere.

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