Tetrahedron Letters,Vol.26,No.34,pp 4125-4128,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

PHOTOREARRANGEMENT OF PHENYL CINNAMATES UNDER MICELLAR ENVIRONMENT[#]

A. K. Singh[*] and T. S. Raghuraman
Department of Chemistry
Indian Institute of Technology
Bombay 400 076, India

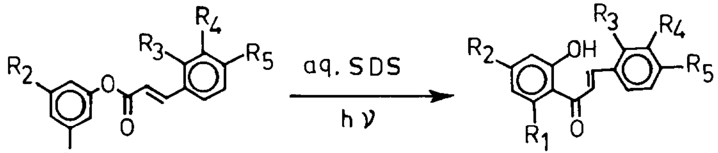
ABSTRACT: Photolysis of phenyl cinnamates in aqueous SDS medium results in an efficient and high yield synthesis of the corresponding 2'-hydroxychalcones.

Micelles as media for chemical reactions present features that are unique in comparision to ordinary non-aqueous or aqueous solvent media. A reaction conducted in micellar media is influenced by the micellar environmental factors such as compartmentalization, localization, pre-orientational, cage, polarity and counter-ion effects. As a result of these effects a high local concentration, longer life time, and reduced translational freedom of the reactive species generated in the micellar environment can be achieved. This is anticipated to bring about catalysis, efficiency, and selectivity in the reactions being done in micellar environment[1].

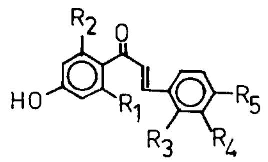
Light induced transformations of phenyl cinnamates leading to isomerization, dimerization, and rearrangement are reported in the literature[2]. The photo-Fries rearrangement of phenyl cinnamate has been exploited for the synthesis of 2'-hydroxychalcones in 20-30 % yield[2]. In general, it is found that the photorearrangement of phenyl cinnamate in common organic solvents yield ortho and para migration products alongwith phenol being the major product. The reaction requires long photolysis time with low overall conversion of the starting material giving low yields. This is apparently because of the fact that the products of the photoreaction, the chalcones, act as internal filters absorbing photons in the region of 350-380 nm. Alternatively, the excited products may quench the reactive triplets of the starting cinnamates.

[#] Dedicated to Professor Koji Nakanishi, Columbia University, New York, on the occasion of his 60th birthday.

In this context and because of our recent findings[3] that aryl esters and N-aryl amides can neatly be converted to the corresponding hydroxy and aminobenzophenones in excellent yields, we undertook the work described in this communication. The present work has led us to a novel, efficient, clean, and high yield transformation of phenyl cinnamates into the corresponding 2'-hydroxychalcones. Phenyl cinnamates 1-6 were prepared according to the procedures described in the literature[2,4]. The 10^{-4} M micellar solutions of the cinnamates were prepared by suspending an appropriate ammount of the cinnamates in 10^{-2} M sodium dodecyl sulfate solution in distilled water followed by stirring for 10-12 hours. The clear micellar solutions were then taken in a quartz immersion well and N_2 was bubbled through it for 10 min. It was then irradiated in an Annular Photoreactor (Applied Photophysics, model APQ 40) having 16 watts low pressure Hg lamp which emmits 90 % light at 254 nm. Irradiation was stopped when no starting material could be detected by tlc. The reaction could also be monitored by observing the disappearence of the ester carbonyl peak at 1725 cm^{-1} and appearence of keto carbonyl peak at 1650 cm^{-1} in the IR spectra. In all the cases photolysis was over within 8 hours. The products were isolated by preparative tlc using silica gel and 10 % ethyl acetate-hexane. The characterization of the products rests upon the comparision of the physico-chemical data (mp, ir, nmr) of these products with that reported in the literature. The results are summarized in scheme I and in the subsequent table.



7, 9, 11, 13, 14, 15



8, 10, 12

1, $R_1 = R_2 = R_3 = R_4 = R_5 = H$

2, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Me$

3, $R_1 = R_2 = R_3 = R_4 = H$, $R_4 = Me$

4, $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = OH$

5, $R_1 = R_2 = OH$, $R_3 = R_4 = R_5 = H$

6 $R_1 = R_2 = OH$, $R_4 = R_5 = OMe$, $R_3 = H$

7, 8, $R_1 = R_2 = R_3 = R_4 = R_5 = H$

9, 10, $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = Me$

11, 12, $R_1 = R_2 = R_3 = R_5 = H$, $R_4 = Me$

13, $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = OH$

14, $R_1 = R_2 = OH$, $R_3 = R_4 = R_5 = H$

15, $R_1 = R_2 = OH$, $R_4 = R_5 = OMe$, $R_3 = H$

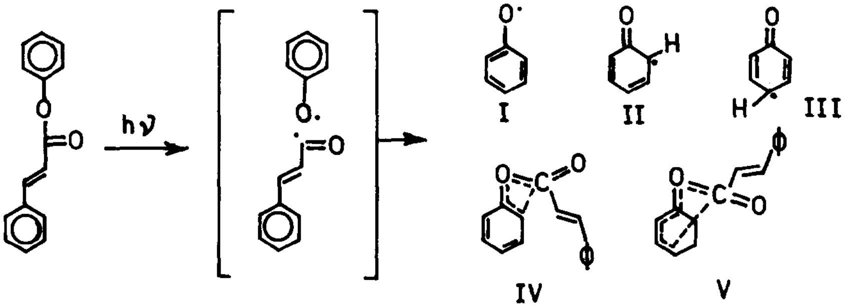
Scheme I

TABLE. Results of Photorearrangement of Cinnamates, 1-6.

Cinnamates	Photoproducts[a]	Cinnamate % Conversion	Product % Yield	Time, hr.
1	2'-Hydroxychalcone, 7	90	70	6
	4'-Hydroxychalcone, 8		15	
2	2-Methyl,2'-hydroxychalcone, 9	90	73	5
	2-Methyl,4'-hydroxychalcone, 10		15	
3	3-Methyl,2'-hydroxychalcone, 11	90	70	7
	3-Methyl,4'-hydroxychalcone, 12		20	
4	2',4'-Dihydroxychalcone, 13	70	70	6
5	2',4',6'-Trihydroxychalcone, 14	75	75	8
6	3,4-Dimethoxy,2',4',6'-trihydroxychalcone, 15	75	75	8

a) All the products were homogeneous by tlc and gave satisfactory mp, ir, and nmr spectral data comparable to those reported in the literature. Yield is based on the material consumed, and is an average of three runs.

These reactions were found to be very clean and required only 5-8 hr of photolysis time giving excellent yields in contrast to the analogous photoreactions in organic solvents[2,5]. There is no indication for the formation of phenol. These results can be explained by considering the analogous photo-Fries rearrangement where it is assumed that the products are formed either from radicals I-III or from intermediates IV and V involving concerted symmetry allowed 1,3 or 1,5 sigmatropic shifts[5](scheme II)



Scheme II

The high yield of the products, short duration of photolysis, and selectivity observed is because of the micellar compartmentalization (protection of the excited state from quenching), preorientational effect (molecules located in the interface region with aromatic group towards the hydrophobic core) and cage effect (restrictiong the translational freedom of the substrate, thus almost freezing the intermediates formed, such as IV).

The formation of $2',6'$-dihydroxychalcone from cinnamate **4** is expected but no such compound could be isolated from the irradiation product. The high conversion of cinnamates is partly because of the use of 254 nm photons where the absorbance by the photoproducts is little. Further, the triplet states of the cinnamates are protected by micellar super cage from quenching. Substituted $2'$-hydroxychalcones serve as biosynthetic precursors to flavonoid and isoflavonoid pigments. Thus this photochemical conversion could serve as a possible model for the biological reaction. Besides, this reaction is a novel alternative for the acylation of phenolic compounds. The Fridel-Craft reaction of phenols with cinnamoyl chloride has been reported[6] to give $2'$-hydroxychalcones which were not stable under the reaction conditions. Thus, the work described herein represents an easy entry into $2'$-hydroxychalcones, not readily available from other methods. The photochemical cis, trans isomerization of olefins is well known but we did not isolate any cis compounds as judged by the coupling constant between the vinylic protons in the nmr. Further, we did not isolate any dimeric product expected to be formed as a result of the 2+2 cycloaddition.

ACKNOWLEDGEMENT: Financial support from the DAE (BRNS Grant No. 37/23/83-G) and CSIR (JRF to T. S. R), Government of India is gratefully acknowledged.

REFERENCES

1. N. J. Turro, M. Gratzel, and A. N. Braun, Angew. Chem. Int. Ed. Engl., **19**, 675 (1980
J. K. Thomas, Chem. Rev., **80**, 283 (1980); J. K. Thomas, Acc. Chem. Res.,**10**, 133(1977)
2. V. T. Ramakrishna, and J. Kagan, J. Org. Chem., **35**, 290 (1970); H. Obara, and H. Tak
hashi, Bull. Chem. Soc. Japan, **42**, 560 (1967); D. N. Dhar, Chemistry of Chalcones and Related Compounds, John Wiley, New York, 1981, p. 12, and references cited therein.
3. A. K. Singh, and S. M. Sonar, Synth. Commun., 1985, in press.
4. A. I. Vogel, A Text Book of Practical Organic Chemistry,3rd edn., ELBS/Longman, London, 1956, p.784.
5. D. Bellus, and P. Hardlovic, Chem. Rev., **67**, 599 (1967); D. Bellus, Advances in Photochemistry, J. N. Pitts, Jr., G. S. Hammond, and W. A. N. Noyes, Jr., eds., Wiley-Interscience, New York, 1971, p. 114, and references cited therein.
6. J. Shinada, and S. Sata, J. Pharm. Soc. Jap., **46**, 791 (1928); ibid., **49**, 71 (1929) and references cited therein.

(Received in UK 10 June 1985)