Modification of photochemical reactivity of *trans*-2-styrylpyridine: effect of cyclodextrin complexation

H. Shayira Banu,[a] A. Lalitha,[a] K. Pitchumani*[b] and C. Srinivasan*[a]

[a] *Department of Materials Science, Madurai Kamaraj University, Madurai -625 021, India.*
E-mail: matsci@pronet.xlweb.com
[b] *School of Chemistry, Madurai Kamaraj University, Madurai -625 021, India*

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In contrast to the solution irradiation of *trans*-2-styrylpyridine, photolysis of a γ-CD complex of the base in the solid state leads to the formation of the *syn*-head-to-tail dimer in fairly good yield.

While irradiation of the free base *trans*-2-styrylpyridine (*trans*-2-SP) under nitrogen in benzene solution leads only to its isomerization to *cis*-2-SP, photolysis of *trans*-2-SP in the solid state in the presence of oxygen yields the dimer in small amounts (2.6%) along with materials formed from photooxidation.[1,2] On the other hand, irradiation of the methiodide and hydrochloride of *trans*-2-SP in the solid state causes ready dimerization; the same process in benzene solution results both in isomerization to its *cis*-form and dimerization. The structure of the dimer has been suggested as one in which the quaternized rings dimerize in alternate positions so as to reduce steric as well as charge interference.[1,2] In another study unimolecular cyclization has been reported[3] during the photolysis of 2-SP in cyclohexane in the presence of oxygen to give benzo[*f*]quinoline in 35% yield, involving the intermediacy of dihydrobenzo[*f*]quinoline along with a minor product 1-phenyl-2-(2-pyridyl)ethanol (10%).

Microheterogeneous media such as micelles, monolayer assemblies, *etc*. are employed to control and achieve some selectivity in the dimerization of 4-styrylpyridinium cations.[4] When salts of 4-styrylpyridinium ions are irradiated in hexane–aerosol OT–water reverse micelles, efficient and selective formation of the *syn*-head-to-head (72%) dimer occurs. This is in contrast to the observation of photolysis in homogeneous solution wherein 13% of the *cis*-isomer and 60% of the *syn*-head-to-tail dimer are produced.[5] When intercalated between the interlayers of clay, 4-styrylpyridinium ions selectively yield the *syn*-head-to-tail cyclodimers.[6]

Cyclodextrins (CDs) are doughnut shaped cyclic oligosaccharides consisting of six, seven or eight glucose units (α-, β- and γ-CDs, respectively) with a hydrophobic inner cavity and a hydrophilic outside. Their cavities have internal diameters varying from 4.7 to 8.3 Å, permitting them to form inclusion complexes with a variety of guest molecules.[7] The depth of the binding cavity of all three CDs is almost the same (7.8 Å). Complexation between CDs and substrates in solution has been successfully exploited to induce selectivity in some unimolecular and bimolecular photochemical reactions.[8] Tamaki and co-workers[9] were the first to explore the utility of the CD cavity in effecting regio- and stereoselective dimerization of guest molecules like anthracene-2-sulfonate and anthracene-2-carboxylate. Photodimerization of acenaphthylene[10] and coumarin[11] upon complexation into the γ-CD cavity has been reported. [2 + 2] Photocycloaddition of a symmetrical stilbene derivative to yield a mixture of dimers in the presence of γ-CD has also been reported.[12] However, inclusion of stilbenes[13,14] in β-CD results in only *cis*–*trans* isomerization, suggesting that the cavity free volume in cyclodextrins plays a major role in controlling the reactivity of the included olefins.

This factor, coupled with the marked observed difference in behaviour during the photolysis of 2-SP and its salt in solution and the solid state, prompted us to study the effect of CD encapsulation on the photochemical behaviour of the free base 2-SP. As the widths of the cavities of α-, β- and γ-CDs increase in a regular manner and therefore the free space available for the guest increases, it is expected that the three CDs will have a varying influence on the photolysis of 2-SP encapsulated in CD. The results of irradiation of 2-SP in the three CDs are presented here.

Irradiation of an MeCN solution of *trans*-2-SP results only in isomerization with the absence of any bimolecular dimerization or unimolecular cyclization in the photostationary state (PSS). A change in the product distribution is noticed when CD complexes of *trans*-2-SP are subjected to irradiation (Table 1).

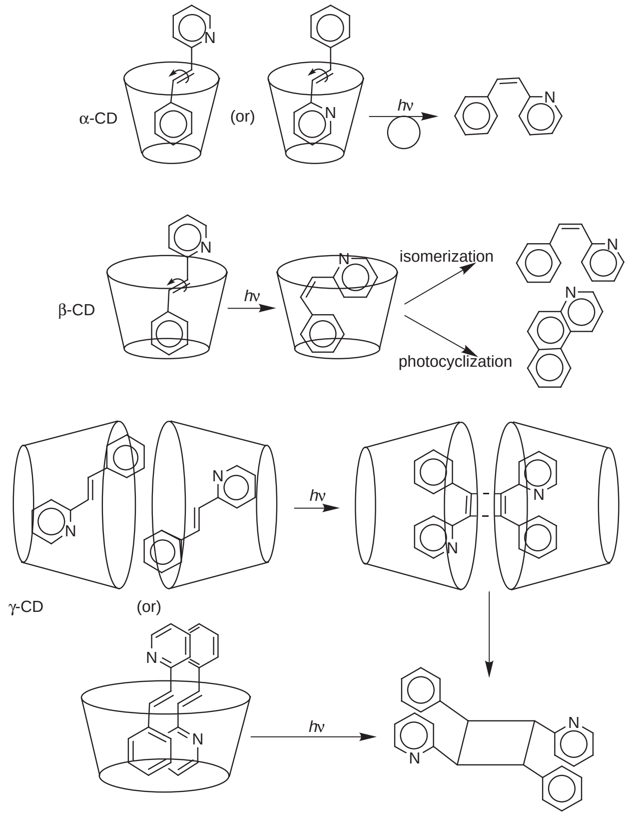
Upon irradiation of a α-CD–*trans*-2-SP complex in the solid state, a dramatic reduction in the percentage of the *cis*-isomer was observed in the PSS compared to the solution irradiation of 2-SP. Because of the smaller width of the α-CD, a restriction is imposed by the α-CD cavity on the photoisomerization of *trans*-2-SP. A small amount of the dimer† is possibly also formed from *trans*-2-SP which has not penetrated significantly into the cavity (Table 1).

The photochemical studies of the solid β-CD complex of *trans*-2-SP reveal not only a decrease in the percentage of *cis*-2-SP, but also a notable increase in the amount of unimolecular cyclized product, benzo[*f*]quinoline (Table 1), at the expense of the *cis*-isomer. The space available in β-CD is large enough to improve *trans*–*cis* interconversion and facilitate the cyclization of the *cis*-isomer. A deeper penetration of the base into β-CD compared to α-CD precludes any contact between two monomers and thus rules out the formation of a dimer. Also the conformation of the *cis*-form in β-CD (Scheme 1) is such that

Table 1 Product distribution on irradiation of *trans*-2-SP in different CDs

Medium	CD : Substrate ratio	*trans*-Isomer	*cis*-Isomer	Dimer	Benzo[*f*]quinoline	X[a]
trans-2-SP in MeCN	—	7	93	—	—	—
trans-2-SP (solid)	—	80	6	5	2	7
α-CD–2-SP (solid)	1 : 1	76	16	6	1	1
β-CD–2-SP (solid)	1 : 1	74	6	1	15	4
γ-CD–2-SP (solid)	1 : 1	31	15	46	6	2
γ-CD–2-SP (solid)	1 : 2	33	7	50	10	—

[a] X = to be identified.



Scheme 1

the dimerization between two *cis*-molecules encapsulated in β-CD may not be easy.

In contrast to the above studies, during the photolysis of a 1:1 γ-CD–*trans*-2-SP solid complex a drastic decrease of *trans*-2-SP in the PSS with prominent formation of the dimer (Table 1) is observed. Since the width of the CD cavity is greatest in γ-CD among the three CDs, this free space is large enough to facilitate a marked increase in *trans*–*cis* photoisomerization. In the 1:1 complex with γ-CD the initially formed *cis*-2-SP can couple with another *cis*-2-SP molecule from the suitably oriented adjacent complex to produce the dimer (Scheme 1). The free space is so large in γ-CD that it can accommodate two molecules of the guest in the cavity of a single molecule of the host and in such a complex efficient photodimerization is expected.‡ Indeed we could prepare a 1:2 complex of γ-CD–*trans*-2-SP and during the photolysis of this solid complex, the yield of the dimer is slightly increased (Table 1). Since the dimer obtained in all the cases studied by us is *syn*-head-to-tail,† we presume that in the 1:2 complex the two *trans*-2-SP molecules are in an antiparallel alignment (Scheme 1).

Thus the observed results are significant as the dimerization is achieved with the free base while earlier reports require quaternization for effective cyclization. The present investigation suggests that it is possible to control the product of photolysis towards either unimolecular (photoisomerization and/or photocyclization) or bimolecular (photodimerization) reactions by choosing the proper CD.

2-SP was prepared and recrystallized as reported in the literature.[15] The dimer (*syn*-head-to-tail) was prepared[1] by the irradiation of 2-SP hydrochloride in benzene as a suspension for 15 h under nitrogen atmosphere using a 365 nm (8 × 8 W) annular photochemical reactor. Benzo[*f*]quinoline was prepared as reported in the literature.[3] α-CD (American Maize products, Indiana), β-CD (Aldrich) and γ-CD (American Maize Products, Indiana) were used as received. The CD complexes were prepared by a procedure reported elsewhere.[16] The CD complexes were irradiated using a 400 W (365 nm) water cooled, immersion type SAIC photoreactor. After irradiation was over, the products were extracted with $CHCl_3$ and the percentage of products were determined by PTLC. The products were characterized by ^{1}H NMR spectroscopy.

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Notes and references

† The dimer obtained in the present study is identified as the *syn*-head-to-tail dimer by its characteristic NMR pattern: $\delta_H(CDCl_3$, 300 MHz) 4.93 (2H, t), 5.10 (2H, t) (cyclobutyl protons), 7.11–7.59 (16H, m, ArH) and 8.66 (2H, d, Ar-H). It is also identified by its characteristic melting point, 189-190 °C (lit. 189–190 °C) (ref. 1,2).

‡ Molecular modelling studies [INSIGHT II (BIOSYM) using the DISCOVER module] were carried out to support the inclusion modes of *trans*-2-SP, *cis*-2-SP, 2 molecules of *trans*-2-SP and *cis*-2-SP inside α-, β- and γ-cyclodextrins. While 1:1 complexes are favoured in α-, β- and γ-CDs inclusion of two molecules of *trans*-/*cis*-2-SP is energetically allowed only in γ-CD. The results support our speculations of preferred modes of complexation. Details of the molecular modelling studies are available from the RSC website, see:http//www.rsc.org/suppdata/cc/1999/607/

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