

Photochemical reactivity of *cis*- or (*Z*)-isomer and *trans*- or (*E*)-isomer of 1-methyl-2-styrylbenzene in homogenous solution at room temperature

Soumya Chatterjee
Department of Chemistry
Rama University, Kanpur, India
guardchem@gmail.com

Abstract— Both the *cis*- or *Z*-isomer and *trans*- or *E*-isomer of 1-methyl-2-styrylbenzene were synthesized and their photochemical reactivity has been studied by irradiation with light from the 300 W ozone free Xenon lamp in methyl-cyclohexane: 2-methyl butane (6:1) homogenous solution at room temperature.

Keywords— Photoisomerization, Stilbenes, Irradiation, Photocyclization

I. INTRODUCTION

Cis-trans photoisomerization of stilbenes and other 1,2-diaryl olefins is thought to occur in the excited singlet state via torsional relaxation about the pertinent bond of which parent stilbenes have been extremely studied [1]. Hommond and Saltiel provided a details understanding of their behavior in the triplet state [2]. Many of the photoisomerizing chromophores (e.g. rhodopsin, bacteriorhodopsin and photoactive yellow protein) reacting exclusively from the excited singlet state [3]. Therefore, studies of mechanistic details of photoisomerization originated from the excited singlet state are of immense interest. Photochemistry of conjugated polyenes has been the subject of considerable study [4-6]. Despite the relative simplicity of the molecules, the results have been quite instructive. One important lesson, pointed out by Havinga and Schlattmann [7] and subsequently elaborated by other researchers [6,8] through their detailed study of the photochemistry of polyenes in the vitamin D series (electrocyclization, sigmatropic rearrangements and geometric isomerizations) was the concept nonequilibrium of excited rotamers which is popularly known as the NEER Principle.

II. MATERIALS AND METHODS

A. Synthesis of *cis*-and *trans*-isomers of 1-methyl-2-styrylbenzene

The *cis*-and *trans*-isomers of 1-methyl-2-styrylbenzene were synthesized by the Wittig reaction of 2-methylbenzaldehyde and benzyltriphenylphosphonium bromide salt [9]. Separation of the isomers was achieved using column chromatography on neutral alumina (Merck) by elution with hexane and monitored through TLC on silica gel GF254 (0.25mm, Merck). The *cis*-and *trans*-isomers of 1-methyl-2-

styrylbenzene were confirmed through ¹H NMR spectroscopy and mass spectroscopy. All the photochemical reactions were performed with the dilute solutions (1x 10⁻³ M) of *cis*- and *trans*-isomer of 1-methyl-2-styrylbenzene in methyl-cyclohexane: 2-methyl butane (6:1) solution at room temperature. Both methyl-cyclohexane and 2-methyl butane used for spectral measurement are of HPLC grade and were procured from Merck, India.

B. Irradiation procedure

The room temperature photochemical setup was made up with an Oxford OptistatDN situated in the cell compartment of a Varian Cary 100 UV-visible spectrophotometer. The Oxford cryotip cell (OptistatDN) was securely fastened in the cell compartment of the UV-visible spectrophotometer. Cylindrical quartz cells were used for the low temperature studies. The sample cells were capped with rubber septum. Irradiation was carried out with a ozone free Xenon 300 W arc lamp. Corning filter plates were used for isolating the desired wavelength for photochemical reactions. Further details on the experimental measurements are reported elsewhere [10].

III. RESULTS AND DISCUSSION

At room temperature both the *cis*-and *trans*-isomer of 1-methyl-2-styrylbenzene were irradiated with light from the 300 W ozone free Xenon lamp in methyl-cyclohexane : 2-methyl butane (6:1) solution and the reactions were followed by UV-visible absorption spectrophotometer.

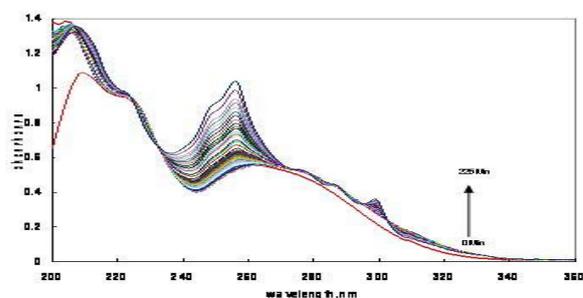


Fig.1. UV-visible absorption spectra of the photoirradiation of *cis*-1-methyl-2-styrylbenzene at room temperature as a function of irradiation time.

The spectra for irradiation of both cis- and trans-isomers of 1-methyl-2-styrylbenzene in methyl-cyclohexane and 2-methyl butane mixture recorded at different irradiation time were given in Fig.1. and Fig.2. respectively. The absorption spectrum of cis-isomer is broad structureless band. Irradiation with light from the Xenon lamp replaced the structureless broad band of cis-isomer by a well resolved vibrational structured band.

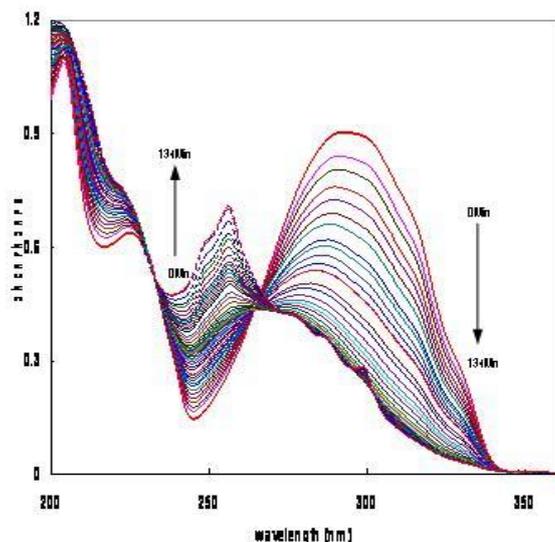
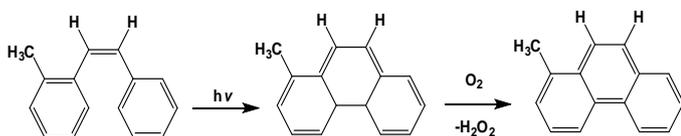


Fig.2. UV-visible absorption spectra of the photoirradiation of trans-1-methyl-2-styrylbenzene at room temperature as a function of irradiation time.

The blue shifted photoproduct suggested that irradiation of cis isomer lead to formation of phenanthrene derivative by two step process. In the first step the cis isomer undergoes photocyclization to form 1-methyl-4a,4b-dihydrophenanthrene and in the second step dihydrophenanthrene is oxidized to form 1-methylphenanthrene (Scheme.1). The preferential cyclization at the expense of isomerization though somewhat surprising, the behavior was observed in many other systems [11,12,13].



Scheme.1. Room temperature reaction path of cis-1-methyl-2-styrylbenzene.

The absorption spectrum of trans-isomer (Fig.2) is broad, less structured and red shifted than the cis-isomer. Upon irradiation using cut-off filter (i.e. with light from > 295 nm) the spectrum is blue shifted and a clear isobestic point is also observed (Fig.2). These changes indicate the conversion of

trans- to cis-isomer and the presence isobestic point in the UV-visible absorption spectra (Fig.2) indicates the simple one to one conversion. After reaching a photostationary state the irradiation was continued by removing the cut-off filter (Fig.2 dotted lines). The spectrum further blue shifted and well resolved vibration structures started to appear which indicate the formation of phenanthrene derivative from cis-1-methyl-2-styrylbenzene.

IV. CONCLUSION

Photoreactivity of both cis (Z) - and trans (E) - isomer of 1-methyl-2-styrylbenzene has been studied in methyl cyclohexane: 2-methyl butane (6:1) homogenous solution at room temperature. The cis-isomer of 1-methyl-2-styrylbenzene undergoes photocyclization at the complete expense of photoisomerization which is surprising. The trans (E) - isomer first undergoes one to one conversion from trans- to cis-. Later on further irradiation without coming filters the cis- undergoes photocyclization to form 1-methylphenanthrene in two step processes.

REFERENCES

- [1] Mazzucato, U., Momicchioli, F., Chem. Rev. 91 (1991) 1679-1719 ; (b) Waldeck, D. H., Chem. Rev. 91 (1991) 415-436.
- [2] Hammond, G. S., Saltiel, J., Lamola, A. A., Turro, N. J., Bradshaw, J. S., Cowan, D. O., Counsell, R. C., Vogt, V., Dalton, C., J. Am. Chem. Soc. 86 (1964) 3197-3217.
- [3] van der Horst, M. A., Hellingwerf, K. J., J. Acc. Chem. Res. 37 (2004) 13-20.
- [4] Saltiel, J., sears, D. F., Jr., D.-H & Pake, K.-M (1995) in Handbook of Photochemistry and Photobiology, eds. Horspool, W. M. & Song, P. -S. (CRC, Boca Raton, FL), pp.3-15.
- [5] Leigh, W. (1995) in Handbook of Photochemistry and Photobiology, eds. Horspool, W. M. & Song, P. -S. (CRC, Boca Raton, FL), pp. 123-142.
- [6] Laarhoven, W. H. & Jacobs, H. J. C. (1995) in Handbook of Photochemistry and Photobiology, eds. Horspool, W. M. & Song, P.-S. (CRC, Boca Raton, FL), pp.143-154.
- [7] Havinga, E., & Schlatmann, J. L. M. A. (1961) Tetrahedron 16, 146-152.
- [8] [8] Jacobs, H. J. C. & Havinga, E., (1979) Adv. Photochem, 11, 305-373.
- [9] Eoin C. Dunne, Éamonn J. Coyne, Peter B. Crowley and Declan G. Gilheany., Tetrahedron Letters 43 (2002) 2449-2453.
- [10] Imamoto, Y., Mishira, K., Tokunaga, K., Kataoka, M., Biochemistry 40 (2001) 14336-14343.
- [11] Krishnamoorthy, G., Schieffer, S., Pescatore, J., Ulsh, R., Liu, R. S. H., Liu, J., Photochem. Photobiol. Sci. 3, 2004, 1047-1051.
- [12] K. Uchida, M. Irie, Photochromism of diarylethylene derivatives, in Handbook of Organic Photochemistry and Photobiology, ed. W. Horspool and F. Lenci, CRC Press, Boca Raton, FL, 2nd edn., 2004, ch. 35, p. 1.
- [13] A. Peters, C. Vitols, R. McDonald, N. R. Branda, Org. Lett. 5, 2003, 1183-1186.