

Triplet Energy Transfer and *Cis-Trans* Isomerization In 3-Phenyl-2-Propenyloxybenzophenone



Kumaresan Murugesan, Sumathi Sowrirajan, Balasubramanian Kalpattu Kuppasamy

Abstract: In this report, photochemical behavior of 2-(3-phenyl-*trans*-2-propenyloxy)benzophenone and 2-(3-phenyl-*cis*-2-propenyloxy)benzophenone is discussed. In contrast to allyl and propargyl ethers of 2-hydroxybenzophenone that were photoactive at 330 nm leading to the formation of 2,3-disubstitutedbenzofuranols, 2-(3-phenyl-*trans*-2-propenyloxy)benzophenone and 2-(3-phenyl-*cis*-2-propenyloxy)benzophenone under these conditions led to photoisomerisation and resulted in the formation of a mixture of *cis* and *trans* isomers in photostationary equilibrium, due to intramolecular energy transfer.

Keywords: Photolysis, Hydroxybenzophenones, Triplet energy transfer, *cis-trans* isomerisation.

I. INTRODUCTION

Hydrogen abstraction reactions¹⁻⁴, hydrogen atom transfer reactions^{1f} and intermolecular energy transfer reactions⁵ in photodecomposition, photo rearrangement, *cis-trans* isomerization, photopolymerization and photoredox reactions play a vital role in organic synthesis. Intramolecular 1,7-hydrogen abstraction and 1,5-biradical cyclisation reaction was the facile photochemical process observed in the solution phase photolysis of allyl / propargyl ethers of 2-hydroxybenzophenones **1**.^{1a,b} Though intermolecular quenching of benzophenone triplet by electron rich/electron deficient alkenes is reported, the intramolecular 1,7-hydrogen abstraction and 1,5-biradical cyclisation reaction of ether **1** in benzene at room temperature, has gone to completion in 40 minutes – 2 hours and 2-ethenyl/ethynyl-3-phenyl-2,3-dihydrobenzofuranols were isolated in 90-95% yield. The later, upon dehydration resulted in the formation of 2-ethenyl/ethynyl-3-phenylbenzofurans **2** in 90% yield (Figure 1). Products due to Paterno-Buchi reaction^{5f}, yet another possible reaction was not observed in the above reaction. The above photochemical

reaction when extended to 2-cyclohexenyloxybenzophenone, spirobenzofuranols as diastereomeric mixture, were isolated in 90% yield. Allyl / propargyl phenyl ethers are well known substrates for photo-Claisen rearrangement.⁶⁻¹⁰ But, ether **1**, though meet the structural requirement for photo-Claisen reaction, it failed to undergo photo-Claisen rearrangement. Surprisingly, *trans* isomer of 5-methyl-2-(3-phenyl-2-propenyloxy)benzophenone **3a** did not undergo the expected intramolecular 1,7-hydrogen abstraction and 1,5-biradical cyclisation. This report describes results of detailed investigation done on the photolysis of 5-methyl-2-(3-phenyl-2-propenyloxy)benzophenone **3a**.

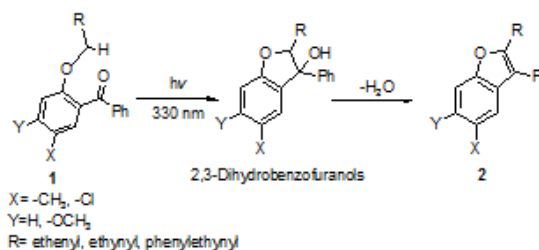


Fig.1 Photolysis of alkenyloxybenzophenones

II. MATERIALS AND METHODS

Photolysis experiments were carried out under oxygen free argon atmosphere in a Rayonet photoreactor RPR 208 model using 350 nm mercury lamps. Solvents and other chemicals used were of laboratory grade. Benzene used for photolysis was purified by following reported procedure.¹¹ Benzene was refluxed and cooled under argon repeatedly thrice before photolysis. Distilled solvents were used for column chromatography. Photo substrates were purified by silica gel (60-120 mesh) column chromatography using benzene-hexane mixture as the eluent. HPLC analysis were carried out on Shimadzu LC 5A unit with UV detector, and aqueous methanol as eluent at the flow rate of 0.4-0.4 mL/min on Zorbax ODS column. ¹H NMR spectra and ¹³C NMR spectra were recorded on Jeol GSX-400 (400 MHz) and Jeol GSX-400 (100.5 MHz) instrument respectively using CDCl₃ as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded using Perkin Elmer 1310 model using CCl₄ as the solvent. Shimadzu 240 spectrophotometer was used for recording the UV spectra.

Revised Manuscript Received on October 30, 2019.

* Correspondence Author

Kumaresan Murugesan*, Research Scholar, Department of Chemistry, Hindustan Institute of Technology and Science, Chennai 603103, India.

Sumathi Sowrirajan, Department of Chemistry, Hindustan Institute of Technology and Science, Chennai 603103, India.

Balasubramanian Kalpattu Kuppasamy, Department of Biotechnology, Indian Institute of Technology Madras, Chennai 600036, India.

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Triplet Energy Transfer and *Cis-Trans* Isomerization In 3-Phenyl-2-Propenyloxybenzophenone

The chemical shifts in NMR spectra are expressed in parts per million from the standard, wavenumbers in IR absorption bands in units of cm^{-1} and wavelength of UV absorption peaks in nanometers and the associated extinction co-efficient are given in parenthesis.

III. RESULTS AND DISCUSSION

The ether **3a** showed R_f value of 0.7 in 2:3 benzene-hexane mixture. IR spectrum of ether **3a** exhibited bands at (cm^{-1}) 2850-3050, 1660, 1600 and 1480. The proton NMR (400 MHz, CDCl_3) of *trans* ether **3a** exhibited the following signals: δ :2.3 (s, 3H, $-\text{ArCH}_3$), 4.58 (dd, $J_{a,b} = 4$ Hz, $J_{a,c} = 1.6$ Hz, 2H, H_a , $-\text{OCH}_2$), 6.0 (td, $J_{b,c} = 16$ Hz, $J_{b,a} = 4$ Hz, 1H, H_b), 6.25 (td, $J_{c,b} = 16$ Hz, $J_{c,a} = 1.6$ Hz, 1H, H_c), 6.9-7.85 (m, 13H, aromatic protons). ^{13}C NMR spectrum (100.6 MHz, CDCl_3) exhibited the following signals at δ : 196.9(s), 154.4(s), 138.3 (s), 136.5 (s), 132.8(d), 132.5 (d), 131.7 (d), 130.5 (s), 130.3 (d), 129.7 (d), 129.2 (s), 128.5 (d), 128.2 (d), 127.7 (d), 126.4 (d), 123.8 (d), 113.1 (d), 68.9 (t), 20.4 (q). The UV absorption spectrum of **3a** recorded in methanol exhibited peaks corresponding to λ_{max} at 250 nm ($\epsilon = 12448$), and 310 nm ($\epsilon = 1366$). Ether **3a** in benzene (10^{-3} M), degassed with Argon, was photolyzed under Argon atmosphere. The reaction was monitored by TLC and High-Performance Liquid Chromatography (HPLC). Even after 10 hours of irradiation, no evidence could be obtained for the formation of 2,3-dihydrobenzofuranol **4a**.

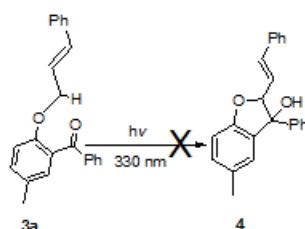


Fig.2 Photolysis of ether **3a**

The high-resolution ^1H NMR spectrum of the photolyzed mass revealed the presence of proton signals corresponding to *cis* and *trans* isomers (2:1) and it was confirmed by comparing the ^1H NMR signals of authentic samples of *trans* (**3a**) and *cis* (**3b**) isomers of 5-methyl-2-(3-phenyl-2-propenyloxy)benzophenone (Figure 3). This was attributed to the photoisomerization of the double bond (Figure 3). It is remarkable to mention here that *trans* (**3a**) and *cis* (**3b**) isomers showed the same retention time in HPLC and had identical mobility in TLC. But both were clearly distinguishable by ^1H NMR spectrum. The details are given below.

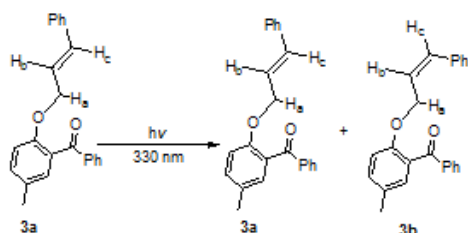


Fig.3 Photoisomerisation in *trans* ether **3a**

The *cis* ether **3b** was prepared by hydrogenation of 5-methyl-2-propenyloxybenzophenone with Lindlar's catalyst in 90 % yield as a pale-yellow liquid. The ether **3b**

also showed R_f value of 0.7 in 2:3 benzene-hexane mixture. IR spectrum of ether **3b** exhibited bands at (cm^{-1}) 2850-3050, 1660, 1600, 1480, 1280 and 700. The proton NMR (400 MHz, CDCl_3) of *cis* ether **3b** exhibited the following signals: δ :2.3 (s, 3H, $-\text{ArCH}_3$), 4.7 (dd, $J_{a,b} = 6.1$ Hz, $J_{a,c} = 1.6$ Hz, 2H, H_a , $-\text{OCH}_2$), 5.52-5.6 (td, $J_{b,c} = 12$ Hz, $J_{b,a} = 6.2$ Hz, 1H, H_b), 6.52 (td, $J_{c,b} = 12$ Hz, $J_{c,a} = 1.6$ Hz, 1H, H_c), 6.8-7.85 (m, 13H, aromatic protons). ^{13}C NMR spectrum (100.6 MHz, CDCl_3) exhibited the following signals at δ : 196.8(s), 153.2(s), 138.5 (s), 136.4 (s), 132.7 (d), 132.3 (d), 132.1 (d), 130.2 (s), 130.1 (d), 129.7 (d), 128.6 (d), 128.3 (d), 128.1 (d), 127.3 (d), 127.1 (d), 123.5 (d), 112.9 (d), 65.5 (t), 20.3 (q). The UV absorption spectrum of **3b** recorded in methanol exhibited peaks corresponding to λ_{max} at 250 nm ($\epsilon = 17400$), and 310 nm ($\epsilon = 1600$).

The ^1H NMR spectrum of photolyzed sample **3a** displayed proton signals characteristic of both *cis* and *trans* isomers (Figure 4). The IR and UV spectral data revealed the presence of carbonyl group. From these results, it is clearly evident that **3a** failed to undergo 1,7-hydrogen abstraction and 1,5-biradical cyclisation but has undergone a facile *cis-trans* isomerization. Irradiation of *cis* isomer **3b** under the current photolysis conditions for 1 hour, also led to a photo-stationary mixture of *cis* and *trans* isomers (1:1). Photolysis of the *trans* isomer **3a** for 1 hour also led to a photo-stationary mixture of *cis* and *trans* isomers (1:1).

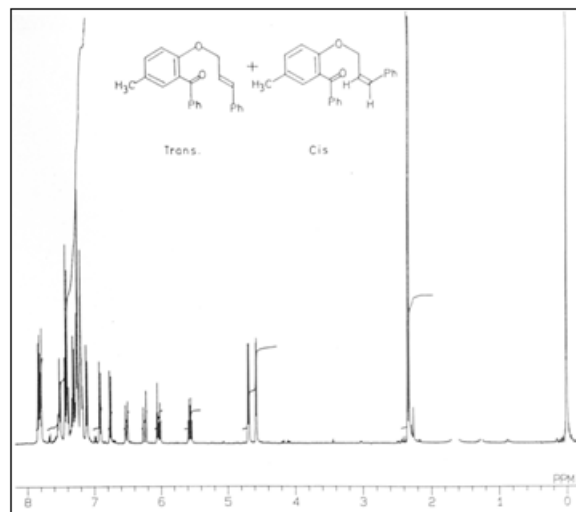


Fig.4 ^1H NMR spectrum of ether **3a** after photolysis

To get a clear picture on whether this geometrical isomerization could have occurred with or without the involvement of carbonyl moiety, 4-methylphenyl 3-phenyl-2-propenyl ether **5** was prepared, characterized by spectral techniques and it was subjected to photolysis at 330 nm for 1 hour. (Figure 5). The NMR spectral data clearly indicated the presence of starting material and there was no evidence for *cis-trans* isomerization.

The Reduction of the *trans* ether **3a** with sodium borohydride in methanol afforded the expected benzylic alcohol **6** (Figure 6). The ¹H NMR spectrum of **6** and the ether **5** revealed the presence of identical proton signals corresponding to 3-phenyl-2-propenyloxy moiety. Further, catalytic reduction ether **3a** (Figure 7) afforded ether **7** which upon photolysis in benzene at 330 nm for 1.5 hours led to 1,7-hydrogen abstraction and 1,5-biradical cyclisation albeit poor conversion (Figure 8). All these evidences, clearly demonstrate the involvement of carbonyl functionality in the *cis-trans* isomerization of ether **3a** and **3b**.

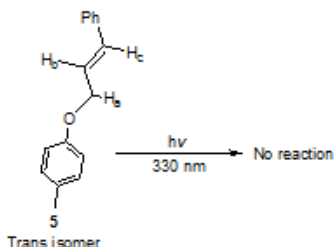


Fig.5 Photolysis of *trans* 4-methylphenyl (3-phenyl-*trans*-2-propenyl) ether

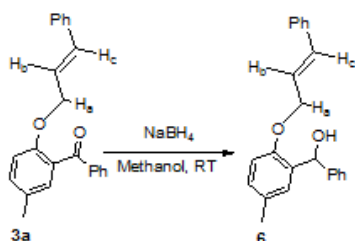


Fig.6 Reduction of ether **3a**

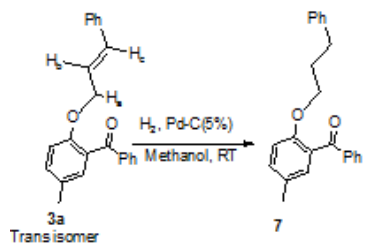


Fig.7 Catalytic reduction of ether **3a**

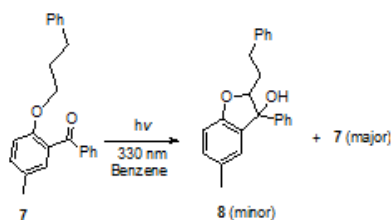


Fig.8 Photolysis of ether **7**

An illustrative example of photochemical *cis-trans* isomerization of alkenes reported in literature¹² is shown below (Figure 9). Further, cinnamic esters¹³ were also reported to undergo *cis-trans* isomerization (Figure 10). In the investigations from our own laboratory on the photolysis of naphthyl analogue of ether **3a** viz. 1-(3-phenyl-*trans*-2-propenyloxy)-2-naphthophenone in benzene at 330 nm, no evidence could be obtained for *cis-trans* isomerization or 1,7-hydrogen abstraction and 1,5-biradical cyclisation. But they undergo photo-Claisen rearrangement, a reaction

occurring from excited singlet state. This may probably due to the fact that the 2-naphthophenone has ($\pi-\pi^*$)³ as the excited state with a decrease in the triplet energy level.^{5c, 14}

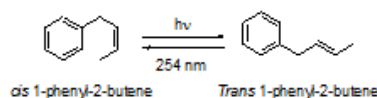


Fig.9 *cis-trans* isomerization in 2-butenes

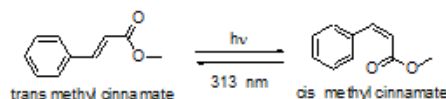


Fig.10 Isomerization in cinnamic esters

It is well known that molecules possessing benzophenone readily form n- π^* triplet as the initial excited state¹⁵. Reactions from excited state will lead to the formation of products. Absence of any photochemical reaction but only photophysical process in ethers **3a** and **3b**, points to a possible quenching of the excited state energy. Based on this, the tendency for *cis-trans* isomerization in preference to 1,7-hydrogen abstraction and 1,5-biradical cyclisation in ether **3a** and **3b** could be attributed to quenching of benzophenone excited state by energy transfer from the triplet carbonyl excited state to the triplet state of double in the 3-phenyl-*trans*-2-propenyl moiety. Triplet energy states in these molecules were not calculated. Assuming that the benzophenone carbonyl moiety in molecules **3a** and **3b** has the triplet energy same as benzophenone ($E_T = 68.5$ kcal/mol)^{5c} and the double bond in 3-phenyl-*trans*-2-propenyl moiety has the triplet energy state same as styrene ($E_T = 62$ kcal/mol).^{1a}

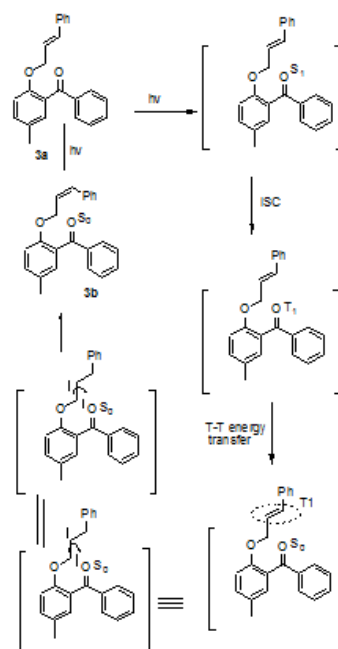


Fig.11 Photo-isomerisation process in ether **3a**

Triplet Energy Transfer and *Cis-Trans* Isomerization In 3-Phenyl-2-Propenyloxybenzophenone

As efficient triplet-triplet energy transfer demands the energy difference between the donor and acceptor triplet states within 7-10 kcal/mol and in the present system, the energy difference is being only

6 kcal/mol, it may be presumed that the *cis-trans* isomerization observed in ethers **3a** and **3b** is purely due to triplet energy transfer process. The 1,7-hydrogen abstraction and 1,5-biradical cyclisation occurs via carbonyl in its excited state. Probably quenching of excited carbonyl triplet by energy transfer also justifies the absence of expected product, 2-(2-phenylethenyl)-3-phenyl-2,3-dihydrobenzofuranol, due to 1,7-hydrogen abstraction and 1,5-biradical cyclisation. Barwise and Gorman¹⁶ in their work on the study of decay of acetophenone triplet in presence of norbornene, have proposed a irreversible triplet energy transfer and from the quantum yield determinations, they have concluded that quenching of the triplet ketone or triplet alkene or the ketone triplet-alkene exciplex by acetophenone occur by processes where there is no energy transfer. Also, in the present work, even prolonged irradiation of ether **3a** only changed the ratio of *cis* / *trans* in the photostationary equilibrium but not made the process irreversible. Based on the above discussions, the photochemical outcome of the irradiation of ethers **3a** and **3b** may be explained as outlined in Figure 11.

IV. CONCLUSION

3-Phenyl-*trans*-2-propenyloxybenzophenone upon photolysis for 1 hour failed to undergo 1,7-hydrogen abstraction and 1,7-biradical cyclisation reaction but underwent photoisomerization leading to photostationary equilibrium containing a 1:1 mixture of *cis* and *trans* isomers. Photolysis of the above ether for a longer time (10 hours) only changed the *cis-trans* equilibrium ratio (2:1). A similar observation was noted in the photolysis of 3-phenyl-*cis*-2-propenyloxybenzophenone. The observed photoisomerization and the absence of any other photochemical reaction was attributed to the intramolecular triplet energy transfer from benzophenone carbonyl moiety to 3-phenyl-2-ethenyl moiety of ether.

ACKNOWLEDGMENT

The authors are grateful to IIT Madras, Chennai for their support in spectral characterization. K. K. B thanks INSA, New Delhi for the award of an INSA Senior Scientist position.

REFERENCES

1. T. Sumathi and K.K. Balasubramanian, *Tetrahedron Lett.*, **1990**, 1, 3775; T. Sumathi (1992) Synthesis and Photo-chemical Studies on ethers of *o*-hydroxybenzo-phenones and Synthesis of Spirobenzofurans (Doctoral dissertation, Indian Institute of Technology Madras, Chennai, India).
(b) T. Sumathi and K.K. Balasubramanian, *Tetrahedron Lett.*, **1992**, 33, 2213.
(c) G.A. Kraus, P.J. Thomas and M.D. Schwinden, *Tetrahedron Lett.*, **1990**, 31, 1819.
(d) M. T. Omirzak, R. Sh. Erkasov, B. G. Sukhov, and T. V. Ganenko, *Russ. Chem. Bull., Int. Ed.*, **2013**, 62, 2442.
(e) P. Wagner. In *Handbook of Organic Photochemistry and Photobiology*, 2nd ed., W. M. Horspool, F. Lenci (Eds.), Chap. 58, CRC Press, Boca Raton (2004). Edward C. Lathioor, William J. Leigh, Photochemistry and Photobiology, **2006**, 82, 291; Cosme G. Francisco, Antonio J. Herrera, and Ernesto Suárez, *J. Org. Chem.*, **2002**, 67, 7439; Angeles Martín, Inés Pérez-Martín, and Ernesto Suárez, *Org. Lett.*, **2005**, 7, 2027
(f) Luca Capaldo, Davide Ravelli, *Eur. J. Org. Chem.*, **2017**, 2056.
2. P. J. Wagner, *Acc. Chem. Res.*, **1989**, 22, 83.
3. E.M. Sharshira, S. Shimada, M. Okamura, E. Hasegawa, T. Horaguchi, *J. Heterocyclic chem.*, **1996**, 33, 1797.
4. E.M. Sharshira, and T. Horaguchi; *J. Heterocyclic chem.*, **1997**, 34, 1837. (b) E.M. Sharshira, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic chem.*, **1997**, 34, 861.
5. (a) V.A. Krongauz, *Russ. Chem. Rev.*, **1966**, 35 678. (b) Q-Q Zhou, Y-Q Zou, L-Q Lu and W-J Xiao, *Angew. Chem. Int. Ed.*, **2019**. <http://dx.doi.org/10.1002/anie.201803102>. (c) R. S. H. Liu, N.J. Turro and G.S. Hammond, *J. Am. Chem. Soc.*, **1965**, 87, 3406. (d) J. C. Scaiano and J. C. Selwyn, *Macromolecules*, **1981**, 146, 1723. (e) R.O. Loutfy, S.K. Dogra and R.W. Yip, *Can. J. Chem.*, **1979**, 57, 342. (f) B. Pintér, F. De Proft, T. Veszprémi and P. Geerlings, *J. Chem. Sci.*, **2005**, 117, 561.
6. M.S. Kharasch, G. Stampa, W. Nudenberg, *Science*, **1952**, 116, 309. (b) F. A. Carroll and G. S. Hammond, *Isr. J Chem.*, **1972**, 10, 613. (c) A. Saito, A. Kanno and Y. Hanzawa. *Angew. Chem.*, **2007**, 119, 4005; P.T. Wong, E.W. Roberts, S. Tang, J. Mukherjee, J. Cannon, A.J. Nip, K. Corbin, M.F. Krummel, and S.K. Choi, *ACS Chem. Biol.*, **2017**, 12, 1001. (d) D.P. Kelly and J.T. Pinhey, *Tetrahedron Lett.*, **1964**, 5, 3427. (e) A.L. Pincock, J.A. Pincock and R. Stenfanova, *J. Am. Chem. Soc.*, **2002**, 124, 9766. (f) K. Schmid and H. Schmid, *Helv. Chim. Acta*, **1953**, 36, 687; H.R. Waespe, H. Heimgartner, H. Schmid, H-J. Hansen, H. Paul and H. Fischer, *Helv. Chem. Acta*, **1978**, 61, 401. (g) G. Pohlers, S. Grimme and H. Dreeskamp, *J. Photochem. Photobiology A; Chem.*, **1994**, 79, 153. (h) G. Koga, N. Kikuchi and N. Koga, *Bull. Chem. Soc. Jpn.*, **1968**, 41, 745. (i) F. Galindo. *J. Photochem. Photobiol. C; Photochem Rev.* **2005**, 6, 123.
7. K. Pitchumani, M. Warriar, V. Ramamurthy, *J. Am. Chem. Soc.*, **1996**, 118, 9428. (b) A.M. Sanchez, A.V. Veglia, R.H. de Rossi, *Can. J. Chem.*, **1997**, 75, 1151.
8. G. Pohlers, S. Grimme and H. Dreeskamp. *J. Photochem. Photobiol. A. Chem.*, **1996**, 95, 41.
9. Y. Suzuki, Y. Okita, T. Morita and Y. Yoshimi, *Tetrahedron Lett.*, **2014**, 55, 3355. (b) C.M. Gonzalez and J.A. Pincock, *Can. J. Chem.*, **2008**, 86, 686. (c) J. T. Pinhey and K. Schafner, *Aus. J. Chem.*, **1968**, 21, 2265. (d) E. Shahbazali, T. Noël, V. Hessel, *J. Flow Chem.*, **2016**, 6, 252.
10. F.A. Carroll, G.S. Hammond, *J. Am. Chem. Soc.*, **1972**, 94, 7151.
11. D.D. Perrin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, Butterworth-Heinemann: 4th edition **1997**.
12. Morrison, H., *J. Am. Chem. Soc.* **1965**, 87, 932.
13. Lewis, F.D., Oxman, J.D., Gibson, L.L., Hampsch, H.L., Quillen, S.L., *J. Am. Chem. Soc.*, **1986**, 108, 3005.
14. (a) M. Yamaji, M. Ogasawara, S. Inomata, S. Nakajima, S. Tero-Kubota, S. Tobita and B. Marciniak, *J. Phys. Chem. A* **2006**, 110, 10708. (b) M. Yamaji, S. Wakabayashi, S. Ueda, H. Shizuka and S. Tobita, *Chem. Phys. Lett.*, **2003**, 368, 41.
15. Z-P Lin and W.A. Aue, *Spectrochimica Acta Part A*, **1999**, 56, 111.
16. A.J.G. Barwise and A.A. Gofwan, *Journal of Photochemistry*, **1978**, 6, 11.