Ultrasound Assisted Greener and Rapid Approach for the Synthesis of Spiro Fluorene with Xanthene Moiety

[1]Rupashri P. Thakur and [2]PramodB. Thakur

[1,2] Department of Chemistry

Rayat Shikshan Sanstha's, Mahatma Phule Arts, Science & Commerce College, Panvel

(Affiliated to University of Mumbai, Mumbai), Raigad, Navi Mumbai, Maharashtra, INDIA

Abstract: *We have demonstrated a new Ultrasound assisted Greener and rapid approach for the synthesis of spiro Fluorene with Xanthene moiety. The synthesis of Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivative was achieved via the condensation reaction of fluorenones with resorcinol using p-toluenesulfonic acid as catalyst under Ultrasound irradiation. The developed method is one-pot synthesis which resulting in to a good yield of the desired product. Short reaction Time, high yield and greener approach are the salient feathers of our methods. This method may applicable for rapid synthesis of series of substituted spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives with halogen, alkyl, phenyl, and ester etc functional groups*

Keywords: Fluorenones, p-Toluenesulfonic acid, Ultrasound Irradiation, Spiro[fluorene-xanthene], Green synthesis

I. INTRODUCTION

In 1895, Thornycroft and Barnaby reported the first phenomenon observed in water after the concept of ultrasound was introduced in 1794: acoustic cavitation [1]. During the movement of the blades, they noticed that the so-called "cavitation events," which involved the formation and implosion of large bubbles, eroded and pitted the propeller of the torpedo boat destroyer HMS Daring. This phenomenon was explained by Rayleigh in 1917 using mathematical models of the vapor bubbles' formation, growth, and collapse in an incompressible fluid [2]. Despite being discovered early on, cavitation was not recognized for its first practical use in chemistry until 1927 by Loomis, Wood, and Richards. For the first time, the chemical effects of high-frequency ultrasound were used to promote particle aggregation, speed up reactions, and even act as a disinfectant [3, 4]. The subsequent growth of sonochemistry was greatly influenced by their work, which became a landmark in the field. In 1934, the first "sono-luminescence" observation was recorded by Frenzel and Schultes. This phenomenon is the cavitation brought on by ultrasonic irradiation that causes light to be released from liquid samples [5]. These findings led to a number of significant advancements in sonochemistry, such as the use of ultrasonography in organic chemistry in 1938 and its influence on electrochemistry in 1935 [6,7]. The widespread application of ultrasonic technology in chemical and biological processes during this period led to the publication of Richards' groundbreaking review paper, "Supersonic phenomena," in 1939 [8].

The potential applications of organic light-emitting diodes (OLEDs) in electrical displays for lighting applications have generated a lot of interest in the optoelectronics community. Over the past 30 years, the OLED industry has expanded dramatically, positioning it as a leading technology today. Optoelectronics research has also peaked in both academia and industry as a result of this. OLEDs also offer new eco-friendly display and lighting technologies. Ongoing research has led to the use of smart OLED devices as a flexible SSL (solid-state lighting) source for smart lighting devices.Recently, OLEDs have gained popularity because of their many amazing features, which make them superior to well-known and established technologies like liquid crystal displays (LCDs). One example of a self-emissive device

is an OLED, which emits light from its pixels without the use of a backlight. LED screens, on the other hand, use a backlight to emit pixels [9]. OLEDs' zero power consumption makes them ideal gadgets as well. Because of this, displays can be lighter, thinner, and "actual (true) black." According to experimental research, OLEDs also have a wide viewing angle, high efficiency, and excellent resolution.Additionally, the display's additional feather increases its flexibility and creates new design options by enabling it to be folded and bent like a roll of paper [10]. However, OLEDs do have certain drawbacks, particularly with regard to material and device structure. First off, most of the materials used to make OLEDs are very inexpensive, but costs can be lowered—possibly even lower than those of LCDs—by changing the structure of the device. As OLEDs continue to improve, there aren't many issues with them at the moment. Another major issue is the short lifespan, which results from lowering the driving voltage.This has been observed, especially with blue OLEDs, which have shorter lifespans than red and green OLEDs but still have sufficient life to provide better resolution and efficiency[11]. In addition, there is always the challenge for scientists to look into the issue of thermal stability in devices.

Furthermore, when creating thermally stable polyesters, spiro compounds with fluorene structures are also used as monomers.31–34 Spiro[fluorene-9,9'-xanthene] (SFX) is a significant class of spirofluorene derivatives that has drawn a lot of interest recently (Figure 1) [12-18]. Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives can be obtained by the condensation reaction of 9-fluorenones with resorcinol using $ZnCl_2/HCl37$ [21] as a condensing reagent at high temperature. SFXs were laboriously synthesized in the early literatures using multistep routes with poor yield [19–20]. Huang [22] reported a quick one-pot method in 2006 to synthesize SFX using a thermodynamically controlled process with an excessive acid catalyst. This method is a practical and effective way to prepare SFX. However, the majority of these techniques are hampered by high temperatures, lengthy reaction times, or the overuse of acidic catalysts. Furthermore, certain processes may result in the introduction of metallic ions or halogens, the amount of which is strictly limited in the preparation of materials. Therefore, it is still very desirable to use the easy way to prepare SFX derivatives in mild conditions. Using p-toluenesulfonic acid as a catalyst, we present an effective one-pot method for preparing spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives. Additionally, this process that eliminates metallic salts and chlorides is better suited to the needs of material research.
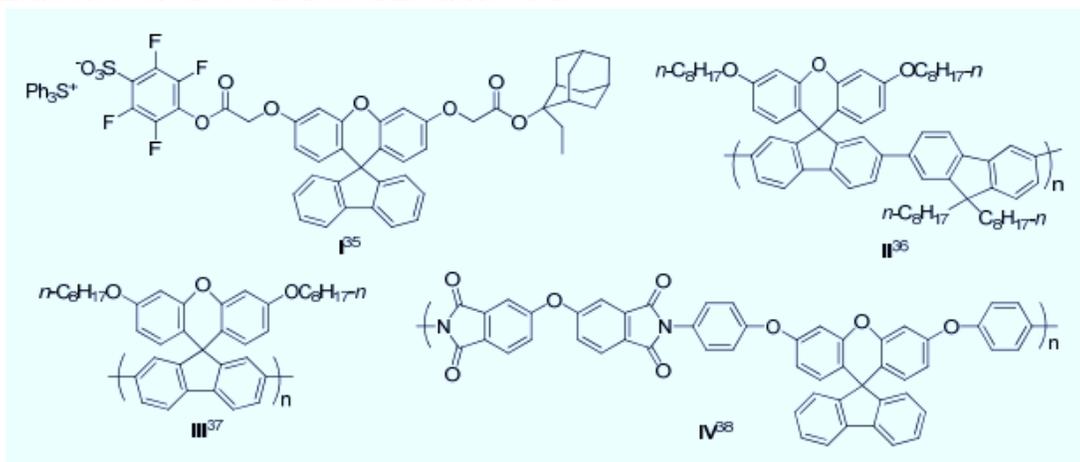

Figure 1: Representative SFX derivatives.

II. RESULTS AND DISCUSSION

At the beginning of work, we have conducted the reaction of one mol of 9-fluorenone (1a) and 2 mole of resorcinol under different reaction conditions (Scheme 1).However we observe that, the reaction was possible and provided the desired product spiro[fluorene-9,9'-xanthene]-3',6'-diol (3a) in good yield, when we used   p-toluenesulfonic acid (p-TsOH) as a catalyst under Ultrasound Irradiation. For initial optimization of the reaction

conditions, we tested several protic acids and Lewis acids, and found the p-toluenesulfonic acid (p-TsOH) gave the best results. Stronger acids such as sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, and polyphosphoric acid (PPA) also served as catalysts, but the yields were relatively low. When sulfuric acid, trifluoromethanesulfonic acid, and PPA were used, the reaction mixtures became dark-brown and many byproducts were generated. Trifluoroacetic acid, aluminum chloride and zinc chloride were not efficient catalysts for the reaction.
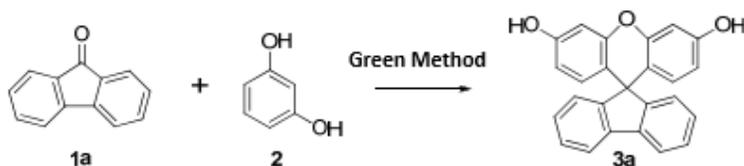
Scheme 1: Optimization of Reaction Condition for the synthesis of Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivative.

As p-TsOH proved to be the most effective acid, further experiments were focused on the screening of solvents. When n-decane and carbon tetrachloride were performed as solvents, dark red gum was generated for poor solubility of resorcinol in these solvents. The conversions were much low when the reactions were carried out in acetic acid, acetonitrile and THF. In all kinds of the tested solvents, toluene and benzene gave the best results. Herein, we do not prefer to choose benzenein view of toxicity. We have also tested the effect of mole of resorcinol on the yield of this reaction. We tested the different mole of resorcinol in this reaction. When we increased the moles of Resorcinol from 3 to 6 mole, we observed the significant increase in the yield of this reaction. The best yield was observed with 6 moles of resorcinol. Hence, we selected reaction of one mol of 9-fluorenone (1a) with6 moles of resorcinol with 10 mol% p-toluenesulfonic acid (p-TsOH) as a catalyst in Toluene solvent under Ultrasound irradiation (32 kHz,) for 1 hr as a optimized reaction condition.
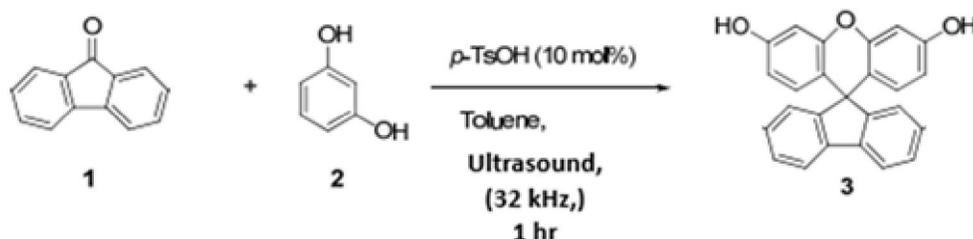
Scheme2: Synthesis of Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivative under Optimized Reaction Conditions.
General Procedure: A mixture of 9-fluorenone (1 mmol) and resorcinol (6 mmol) was prepared in 10 ml Toluene at room temperature (25^0C). The reaction mixture was then exposed to ultrasonic irradiation of frequency of 32 kHzusing an ultrasonicator probe. The progress of the reaction was monitored using thin-layer chromatography (TLC). After 1hr,precipitate was collected by filtration, dried. The obtained crude product was dissolved into alcohol (10 mL) and filtrated to remove insoluble impurity (4). The organic solution was concentrated, purified by chromatography on silica gel using petroleum ether/EtOAc (3:1) as an eluant, and dried to afford product 3 as a white solid. The pure product was confirmed by different techniques and identified as Spiro[fluorene-9,9'-xanthene]-3',6'-diol.

Spectral Data: Spiro[fluorene-9,9'-xanthene]-3',6'-diol (3).15 White solid, yield 90%, 918 mg; mp 262-264 °C, m/z: 363 ([M–H]-), 399 ([M+Cl]-); ^{1}H NMR (400 MHz, DMSO-d6) δH: 9.63 (s, 2H, OH), 7.92 (2H, d, 3 JHH 7.6 Hz, ArH), 7.36 (2H, t, 3 JHH 7.6 Hz, ArH), 7.22 (2H, t, 3 JHH 7.6 Hz, ArH), 7.02 (2H, d, 3 JHH 7.6 Hz, ArH), 6.59 (2H, d, 4 JHH 2.0 Hz, ArH), 6.26 (2H, dd, 3 JHH 8.8 Hz, 4 JHH 2.0 Hz, ArH), 6.03 (2H, d, 3 JHH 8.8 Hz, ArH).

III. CONCLUSION

In conclusion, we have demonstrated new rapid and greener method for synthesizing spiro fluorene with a xanthene by condensation of fluorenones with resorcinol using p-toluene sulfonic acid moiety using ultrasound assistance. In this method, Spiro[fluorene-9,9'-xanthene]-3',6'-diol derivative was synthesized as a catalyst under ultrasound irradiation. This is One-pot synthesis which gives goodamount of yields of the desired product in short reaction time. Our methods stand out for their short reaction time, high yield, and environmentally friendly approach. Furthermore, this method can be applicable to synthesize a number of substituted spiro[fluorene-9,9'-xanthene]-3',6'-diol derivatives with different functional groups such as halogen, alkyl, phenyl, and ester.

IV. ACKNOWLEDGMENT

REFERENCES

[1]. J. I. Thornycroft and S. W. Barnaby, *Journal of the American Society for Naval Engineers*,1895, **7**, 711-736.

[2]. L.Rayleigh,*TheLondon,Edinburgh,andDublinPhilosophicalMagazineandJournalof Science*, 1917, **34**, 94-98.

[3]. R. W. Wood and A. L. Loomis, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 1927, **4**, 417-436.

[4]. W.T.RichardsandA.L.Loomis,*Journal oftheAmericanChemical Society*,1927,**49**,3086- 3100.

[5]. H.FrenzelandH.Schultes,*ZeitschriftfürPhysikalischeChemie*,1934,**27B**,421-424.

[6]. B. Von Claus, *Z. Tech. Phys.*, 1935, **16**, 80-82.

[7]. C.W.PorterandL.Young,*JournaloftheAmericanChemicalSociety*,1938,**60**,1497-1500.

[8]. W.T.Richards,*ReviewsofModernPhysics*,1939,**11**,36-64.

[9]. Motoyama, Y.; Sugiyama, K.; Tanaka, H.; Tsuchioka, H.; Matsusaki, K.; Fukumoto, H. *J. Soc. Inf. Disp.* 2019, **27**, 354.

[10]. Cooper, E. A.; Jiang, H.; Vildavski, V.; Farrell, J. E.; Norcia, A. M. J. V*isualization* 2013, **13**, 16.

[11]. Kalyani, N. T.; Dhoble, S. J. *Renewable Sustainable Energy Rev.* 2015, **44**, 319.

[12]. Kasai, T.; Higashihara, T.; Ueda, M. *J. Appl. Polym. Sci.* 2014, **131**, 39769.

[13]. Carbas, B. B.; Asil, D.; Friend, R. H.; Önal, A. M. *Org. Electron.* 2014, **15**, 500–508.

[14]. Tseng, Y. H.; Shih, P. I.; Chien, C. H.; Dixit, A. K.; Shu, C. F.; Liu, Y. H.; Lee, G.. H. *Macromolecules* 2005, **38**, 10055–10060.

[15]. Zhang, S.; Li, Y.; Ma, T.; Zhao, J.; Xu, X.; Yang, F.; Xiang, X.-Y. *Polm. Chem.* 2010, **1**, 485–493.

[16]. Pietraszkiewicz, M.; Maciejczyk, M.; Samuel, I. D. W.; Zhang, S. *J. Mater. Chem. C* 2013, **1**, 8028–8032.

[17]. Poriel, C.; Rault-Berthelot, J.; Thirion, D. *J. Org. Chem.* 2013, **78**, 886–898.

[18]. Chen, M.; You, Y.; Zhang, Y.; Li, H.; Fang, W. *Chem. J. Chinese* U. 2014, **35**, 63–67.

[19]. Walters, M. E.; Richey, W. F.; Clement, K. S.; Brewster, S. L.; Tasset, E. L.; Puckett, P. M.; Durvasula, R. Nguyen, H. A. US 5387725, 1995; *Chem. Abstr.* 1995, **123**, 198448.

[20]. Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* 1930, **52**, 2881–2891.

[21]. Bischoff, F.; Adkins, H. *J. Am. Chem. Soc.* 1923, **45**, 1030–1033.

[22]. Xie, L. H.; Liu, F.; Tang, C.; Hou, X. Y.; Hua, Y. R.; Fan, Q. L.; Huang, W. *Org. Lett.* 2006, **8**, 2787–2790.