Impact Factor Value 4.046 **e-ISSN: 2456-3463**
International Journal of Innovations in Engineering and Science, Vol 4, No.10,2019
National Level Technical Paper Presentation- PHOENIX-19
Organized by Godavari College of Engineering, Jalgaon- 425003
www.ijies.net

Synthesis of 14-aryl-14-H-Dibenzo(a,j) Xanthene using Citric Acid

[1]BoroleHarshalTukaram, [2]JayashriDinkarBhirud
[1]BoroleHarshalTukaram(M.Sc.) , [2]Jayashri D. Bhirud
[1]PG student,[2]Assistant professor
[1,2]Department Of Chemistry, MooljiJaitha College, Jalgaon, India,425002
harshucb123@gmail.com[1],ingale.jayashri@rediffmail.com[2]

Abstract- *An efficient and simple method have been developed for the synthesis of biologically active 14-aryl-14H-dibenzo[aj]xanthenesthrough one pot condensation of aryl aldehydes and β-napthol under solvent-free conditions in the presence of Citric acid as an efficient solid acid catalyst with excellent yields and short reaction time.*

Keywords-β-Naphthol, Xanthene, Citric acid, alum, Tumarind juice

1. INTRODUCTION

The synthesis of xanthenes is important is organic synthesis because of their wide range of biological and pharmaceutical properties.Xanthenes derivatives having various biological and therapeutic properties including antibacterial[1], anti-inflammatory[2], antiviral[3], and ant proliferative[4], anti neo plastic activities[5].As well as due to their application in photodynamic therapy[6], these heterocyclic entices are widely used as dye[7], in laser technology[8] and pH sensitive fluorescent materials[9-11] [1-11]. Many methods for the synthesis of xanthenes derivatives have been reported. However many of these methods suffer from one or more disadvantages such as long reaction times, harsh reaction condition, tedious workup use of toxic solvents and expensive reagents. Thus there is a need for development of an alternative route to synthesis the xanthenes derivatives. Therefore we have to develop simple and efficient way to synthesized xanthene derivatives by using citric acid as a catalyst.

2. EXPERIMENTAL METHODS

To the mixture of substituted benzaldehyde (1 mmol) and 2-naphthol (2mmol), Citric acid (5mol %) was added and reaction mixture was stirred at 120°Cfor appropriate time. The progress of reaction was monitored by TLC. After completion of the reaction, water (10ml) was added and the mixture was stirred for 10 min. The obtained solid was collected by filtration and purified by re- crystallization from ethanol.

R=4-BrC_6H_5 , 4-$NO_2C_6H_5$, 2-ClC_6H_5, C_6H_5, 4-$OCH_3C_6H_5$, 4-$NMe_2C_6H_5$

Scheme-1

3.1Materials and methods

^{1}H NMR spectra were recorded in DMSO-d_6/$CDCl_3$ using Bruker AVANCE II 400 NMR spectrometer with resonating frequency 400 MHz. Mass spectra were recorded on WATERS Q-TOF MICROMASS (LC-MS) (SAIF, Panjab University, Chandigarh). FT-IR spectra were recorded using Schimadzu IR affinity model-1 spectrometer. Progress of reaction was monitored by TLC in chloroform: ether system (80:20).

3.2. Physical and spectral data

14-(4-bromophenyl)-14H-dibenzo[a,j]xanthene (3a): White solid: mp 302–303°C. IR (KBr, cm^{-1}): 3089, 1623, 1590, 1446, 1235, 1088, 814, 751. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): ó 6.40 (s, 1H), 6.81 (d, 2H, J = 8.1 Hz), 7.19 (d, 2H), 7.34–8.45 (m, 12H); Mass (m/z): 436.

14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene (3b): Yellow solid: mp 311–313°C. IR (KBr, cm^{-1}): 3069, 1604, 1560, 1389, 1267, 1122, 815, 745; 1H NMR (400 MHz, $CDCl_3$, ppm): 6.70 (s, 1H, CH), 7.20–7.25 (2H, m, Ar-H), 7.31–7.40 (2H, d, Ar-H), 7.53–7.60 (2H, d, Ar-H), 7.65–7.80 (4H, m, Ar-H), 7.93 (s, 2H, CH), 8.25–8.54 (4H, d, Ar-H). Mass (m/z): 403.

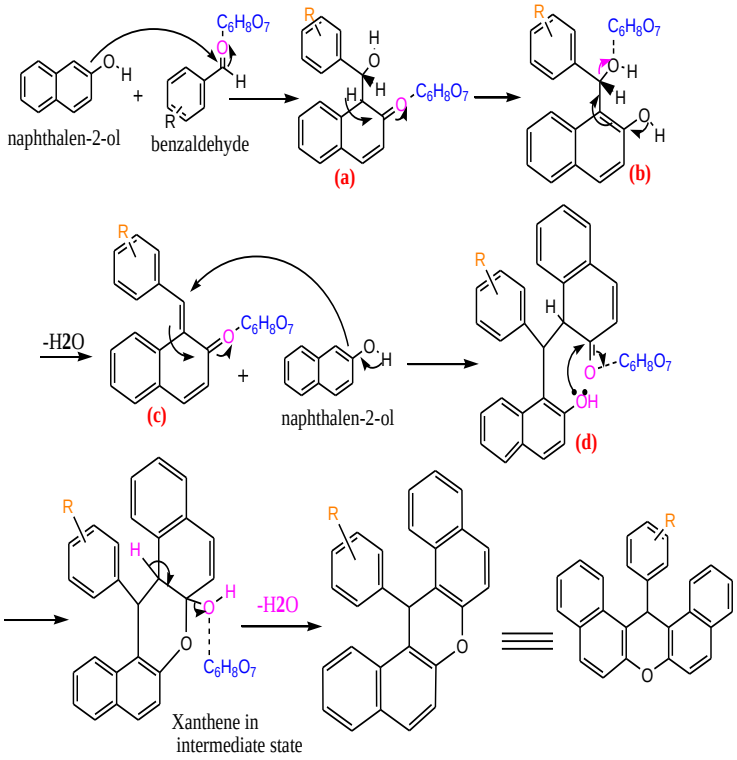
14-(2-Chlorophenyl)-14H-dibenzo[a,j]xanthene (3c): White solid: mp 214–216°C. IR (KBr, cm^{-1}): 3047, 1625, 1567; 1517, 1089, 875. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ó 6.85(s, 1H),

7.05–7.14 (4H, m, Ar-H), 7.25-7.32 (dd, 2H), 7.40–7.46 (4H, m, Ar-H), 7.56–7.60 (4H, d, Ar-H), 7.84–7.94 (2H, m, Ar-H), Mass (m/z): 394 (M+2), 392(M).

14-(phenyl)-14H-dibenzo[a,j]xanthene (3d): White solid: mp 183–185°C. IR (KBr, cm^{-1}): 3037, 2911, 1667, 1542, 1478, 1242, 1098, 867. ^1H NMR (400 MHz, $CDCl_3$, ppm): ó 6.67 (s, 1H), 7.10-7.24 (t, 1H, ArH), 7.35-7.43(d, J=8 Hz, 2H, ArH), 7.47–7.69 (m, 7H, ArH), 7.80–7.89 (m, 5H, ArH), 8.43 (d, 2H, ArH); Mass (m/z): 358.

14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (3e): White solid: mp 224–227°C. IR (KBr, cm^{-1}): 3078, 1615, 1576, 1441, 1256, 790, ^1H NMR (400 MHz, $CDCl_3$, ppm): ó 2.41 (s, 3H), 6.67 (s, 1H), 6.89 (2H, d), 7.10-7.27 (8H, m), 7.56-7.78 (4H, m), 7.86 (2H, dd), Mass (m/z): 388 (M^+).

14-(N,Ndimethylaniline)-14H-dibenzo[a,j]xanthene (3f): White solid: mp 299–301°C. IR (KBr, cm^{-1}): 3067, 1653, 1545, 1223, 1068, 887. ^1H NMR (300 MHz, $CDCl_3$, ppm): ó 6.67 (s, 1H), 7.25 (d, 2H), 7.66–8.89 (m, 20H); Mass (m/z): 401.



Scheme-2: General Mechanism

Figure-1: TLC of Product**(3a)**

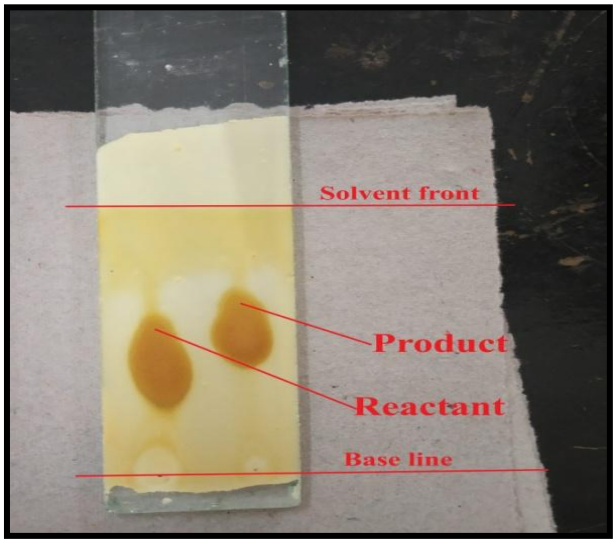


Figure-2: FT-IR Spectraof Product**(3a)**

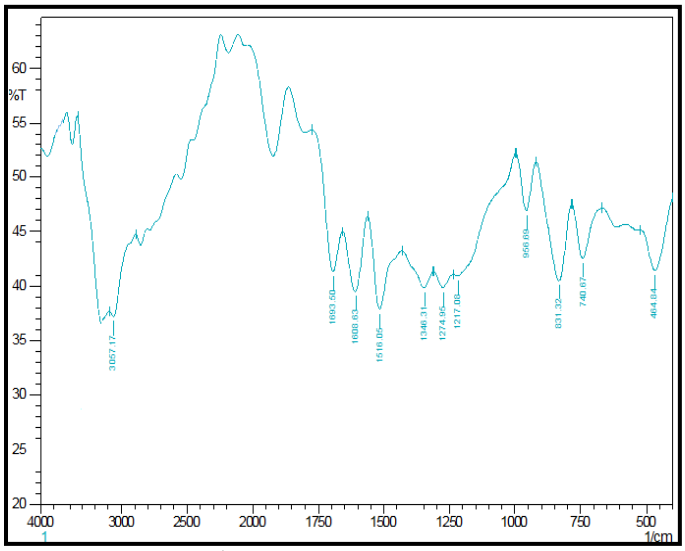


Figure-3:^1H NMR Spectra of Product**(3d)**

Figure-4: Reactions

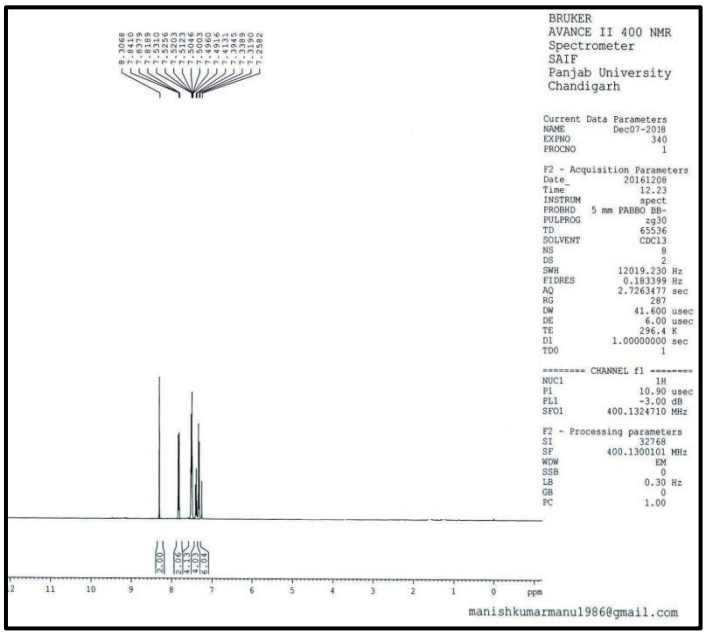


Figure-5 Effects

4. RESULT AND DISCUSSION

We started to study this condensation reaction using a catalytic amount of alum, tamarind juice and citric acid by examining the reaction times and yield involving 4-bromobenzaldehyde (1 mmol) and 2-naphthol (2 mmol) to afford the product under solvent-free conditions at 120°C (Table 1). As can be seen from Table 1, the best results were obtainedat 5mol% of the citric acid as catalyst under solvent-free conditions and gave 14-(4-bromophenyl)-14H-dibenzo[a,j]xanthene in 95% yield in 30 minutes. The catalyst played a crucial role in the accomplishment of the reaction in terms of time and the yields.

Table-1 Effect of catalyst on yield of (14-(4-bromophenyl)-14H-dibenzo[a,j]xanthene (3a)

Sr.No.	Catalyst	Time (min)	Yield
1	Alum	120	69
2	Tamarind Juice	80	58
3	Citric Acid	30	95

5. CONCLUSION

We have reported the synthesis of 14aryl-14H-dibenzo xanthenes in the presence of Citric acid under solvent free conditions at 120°C. This method is simple effective, short reaction time, excellent yield at solvent free condition.The catalyst is inexpensive and conveniently removed. The method used in the present work proved to be convenient economical and eco-friendly as no other byproduct was formed and no toxic material was used during synthesis.

6.REFERANCES

[1] *G. MohammadiZiarani, A., R. Badiei M. Azizi, The one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives using sulfonic acid functionalized silica (SiO2-Pr-SO_3H) under solvent free conditions , ScientiaIranica, 18 (3), 453–457, 2011.*

[2] *J. P. Poupelin, G. Saint-Rut, O. Fussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, and R. Lakroix, "Synthesis and anti-inflammatory properties of bis (2-hydroxy-1-naphthyl)methane derivatives I," European Journal of Medicinal Chemistry, vol. 13, pp. 67–71, 1978.*

[3] *T. Hideu, "Benzopyrano[2,3-b]xanthene derivatives," Jpn. TokkyoKoho JP 56005480, Chemical Abstracts 95, 80922b, 1981.*

[4] *R.W. Lamberk, J. A.Martin, J.H.Merrett,K.E.B.Parkes, andG. J. Thomas, PCT International Applications WO 9706178, 1997, Chemical Abstracts 126, P212377y, 1997.*

[5] *S. L. Niu, Z.-L.Li, F. Ji et al., "Xanthones from the stem bark of Garciniabracteata with growth inhibitory effects againstHL-60 cells," Phytochemistry, vol. 77, pp. 280–286, 2012.*

[6] *F. K. Behbahani ,M.Valiallahi, Synthesis of 14-aryl-14H-dibenzo[a,j]xanthenesusing CuSO4Æ5H2O as a green and reusable catalyst, Arabian Journal of Chemistry ,10, S1686–S1689, 2010.*

[7] *G. L. N. Djoufack, K. M. Valant-Vetschera, J. Schinnerl, L. Brecker, E. Lorbeer, and W. Robien, "Xanthones, biflavanones and triterpenes from Pentadesmagrandifolia(Clusiaceae): Structural determination and bioactivity," Natural ProductCommunications, vol. 5, no. 7, pp. 1055–1060, 2010.*

[8] *N. Hashim, M. Rahmani, M. A. Sukari et al., "Two new xanthones from Artocarpusobtusus," Journal of Asian NaturalProducts Research, vol. 12, no. 2, pp. 106–112, 2010.*

[9] *P.Moosophon, S. Kanokmedhakul, K. Kanokmedhakul, and K. Soytong, "Prenylxanthones and a bicyclo[3.3.1]nona-2,6-diene derivative from the fungus Emericellarugulosa," Journal ofNatural Products, vol. 72, no. 8, pp. 1442–1446, 2009.*

[10] *S.J. Tao, S.-H.Guan,W.Wang et al., "Cytotoxic polyprenylatedxanthones from the resin of Garciniahanburyi," Journal ofNatural Products, vol. 72, no. 1, pp. 117–124, 2009.*

[11] *G. B. Azebaze, M. Meyer, A. Valentin, E. L. Nguemfo, Z. T. Fomum, and A. E. Nkengfack, "Prenylatedxanthone derivatives with antiplasmodial activity from AllanblackiamonticolaStaner L.C.," Chemical and Pharmaceutical Bulletin, vol. 54, no. 1, pp. 111–113, 2006.*