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Research Paper

Microwave Assist Green Synthesis of 12-Alkyl Or Aryl-8, 9, 10, 12 - Tetrahydrobenzo [A] Xanthen-11-Ones

Chemistry

KEYWORDS :

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ABSTRACT

The ideology of green chemistry calls for the development of new chemical reactivities and reaction conditions that can potentially provide benefits for chemical synthesis in terms of resource efficiency, energy efficiency, product selectivity, operational simplicity, ease of work-up and product isolation and last but not least the health and environmental safety. In green synthesis, the organic solvents are replaced by green solvents under microwave condition in solvent free condition.

Compounds bearing xanthenes and benzoxanthene are ubiquitous to a variety of biologically important natural products and drugs. They possess various biological activities such as anti-inflammatory[8] antiviral[9] and antibacterial[10]. Some of them have been used as antagonists for paralyzing the action of zoxazolamine and in photodynamic therapy[11]. These compounds exhibit industrial application also especially for the production of organic dyes [12] and pH-sensitive fluorescent materials [13].

INTRODUCTION

The ideology of green chemistry calls for the development of new chemical reactivities and reaction conditions that can potentially provide benefits for chemical synthesis in terms of resource efficiency, energy efficiency, product selectivity, operational simplicity, ease of work-up and product isolation and last but not least the health and environmental safety. In green synthesis, the organic solvents are replaced by green solvents under microwave condition in solvent free condition.

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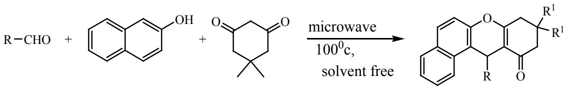
Recently enormous progress has been made in expanding the scope of condensation of β-naphthol, aldehyde with 1,3-dicarbonyl compounds for synthesis of 12-aryl or 12-alkyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one derivatives by employing a wide array of catalysts such as triethylbenzylammonium chloride (TEBA**)** [14]**,** $NaHSO_4$-SiO_2 [15]**,** strontium triflate [16]**,** tetrabutylammonium fluoride (TBAF) [17], molecular iodine [18], Indium trichloride [19] etc. ionic liquid [20]) and Zwitterionic-Type Molten Salt [21] also been used as the catalyst for the following transformations.

AIMS & OBJECTIVES

- Green synthesis of 12-aklyl or aryl-8,9,10,12-tertrahydro[a] xanthen-11-ones derivatives under microwave conditions avoiding toxic reagents & solvents & optimized the desired product.
- After optimization, we next examined the generality of the reaction condition to other substrates using several aromatic aldehydes.
- Confirmation of the desired product by checking melting point & also by studying IR,1H NMR & 13C NMR Spectroscopy.

PRESENT WORK

During our project work, we have developed a simple and efficient method for the synthesis of 12-alkyl or aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives by three-component coupling of β-naphthol, aldehyde and dimedone under microwave condition (Scheme 1).



Scheme 1

Firstly we have optimized the reaction. To optimize the reaction conditions, the reaction of β-naphthol, benzaldehyde and dimedone was selected as model to examine the effects of catalyst (0-20%).The results were summarized in Table-1 and evaluated qualitatively. The best result was achieved by carrying out the reaction with 1:1:1 mole ratios of β-naphthol, benzaldehyde and dimedone under microwave condition.

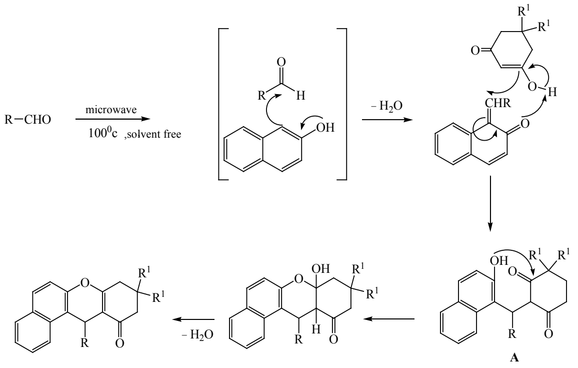
Table 1. Optimization in different condition of microwave irradiation on the reaction of 2-naphthol, benzaldehyde and dimedone

Entry	temperature ^{0}c	Time (min)	Yield (%)
1	45	5	<5
2	85	10	60
3	99	10	84
4	**100**	**25**	**86**
5	90	30	80

After optimization, we next examined the generality of the reaction condition to other substrates using several aromatic aldehydes. The results are summarized in Table 2. In all cases, aromatic aldehydes containing either an electron- withdrawing group or an electron-donating group reacted successfully and gave the products with all most same yields. Evaporation of solvent furnished the crude product and recrystalisation in ethanol give the pure product.

THE POSSIBLE MECHANISM

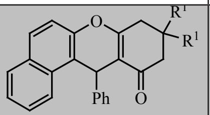
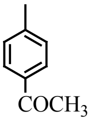
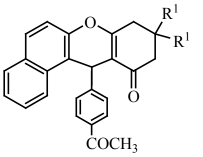
The possible mechanism of this reaction is shown in Scheme 2. The condensation of 2-naphthol with aldehydes is believed to proceed *via ortho*-quinone methide intermediates (*o*-QMs) [22]. Then, the trapping of *o*-QMs with dimedone formed intermediates A, which were cyclized and then dehydrated to give the corresponding xanthene derivatives.



Scheme 16 Hypothetical mechanism for the synthesis of xanthene-based compounds

MY EXTENSION WORK : In the microwave assist green synthesis of the xanthen we used a perticuler aldehyde .Now we have tried to use deffernt aldehyde with different group. And as we used the defferent aldehyde we get defferent functionalized xanthen .Here the table is....

Table 2

-R groups of the aldehyde	Xanthen	Temperature (0c)	Time **(min)**	Yield **(%)**
-ph		**96**	**28**	78
		**110**	**30**	**65**

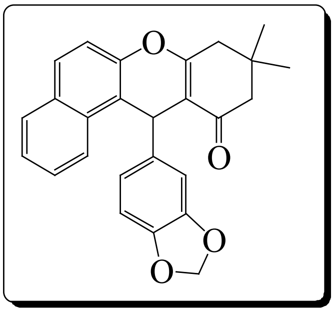
II.3.6 EXPERIMENTAL :-

General: Melting points were determined on a glass disk with an electrical bath and are uncorrected. IR spectra were recorded on a FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ solution operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. NMR spectra recorded on a Chemical shift were recorded as δ values in parts per million (ppm), and were indirectly referenced to trimethylsilane (TMS) *via* the solvent signal. The signals were reported as a s = singlet, d = doublet, t = triplet, m = multiplet and coupling constant are given in Hz. Thin layer chromatography was done on silica gel coated aluminum plate (Merck). All the liquid substrates were distilled before use. Solvents, reagents and chemicals were purchased from Merck, SRL, Spectrochem and SQ.

General procedure for 12-alkyl or aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones:

A mixture of β-naphthol (2 mmol), aldehyde (2 mmol) and dimedone (2 mmol) was taken in a round bottom flask with 3 ml of methanol under microwave condition. The reaction mixture was stirred at room-temperature for a certain period of time as required to complete (TLC). After completion, the reaction mixture was extracted with ethyl acetate (10 mL X 3), then the organic layer were washed firstly with dil. NaOH solution(10 mL X 3) and then with brine(10 mL X 3). Evaporation of solvent furnished the crude product. The crude product is recrystallized from hot ethanol to obtain analytical pure products.

Spectral and analytical data of 12-Benzo[1,3]dioxol-5-yl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (entry):



White solid; mp.189-190 ^{0}C;

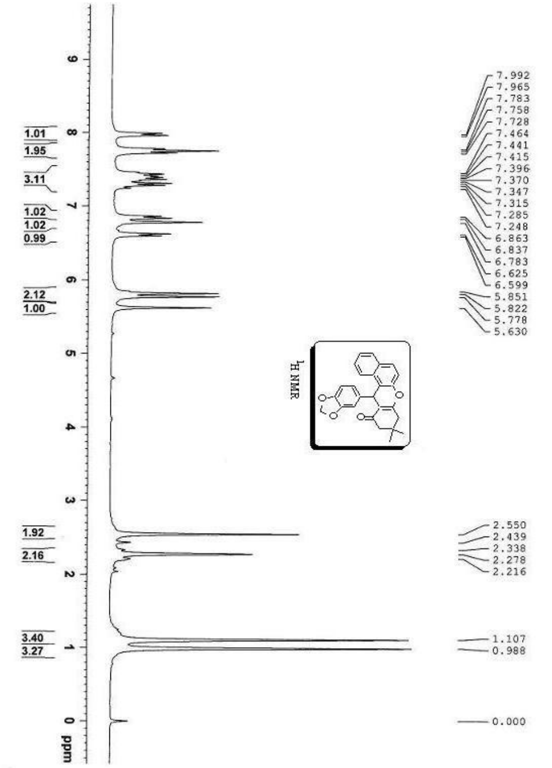
IR (KBr): 2957, 2877, 1648, 1474, 1375, 1176, 1029 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.46-7.25 (m, 3H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 5.82 (s, 1H), 5.77 (s, 1H), 5.63 (s, 1H), 2.55 (s, 2H), 2.27 (s, 2H), 1.10 (s, 3H), 0.98 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 163.6, 147.5, 147.3, 145.6, 138.7, 131.3, 131.2, 128.7, 128.3, 126.8, 124.8, 123.5, 121.6, 117.5, 116.9, 114.1, 108.8, 107.8, 100.6, 50.8, 41.2, 34.2, 32.1, 29.1, 27.1;

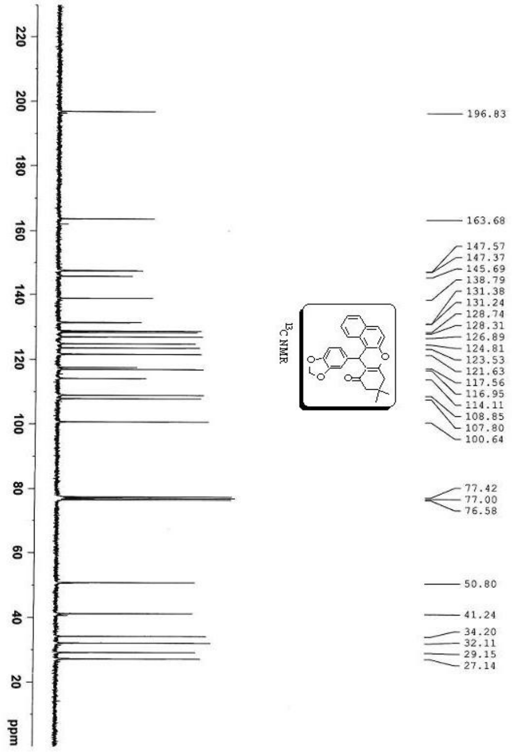
II.3. 6CONCLUSION :-

In summary, we have described an efficient protocol for the synthesis of 12-alkyl or aryl-8,9,10,12-tetrahydro[*a*]xanthen-11-one derivatives under microwave condition. The main advantages of this procedure are: (a) simple operation; (b) good yields–(c) general applicability; (d) above all, green synthesis avoiding toxic reagents and solvents.



Part II

Section III ------------------------------------



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