

Novel catalytic application of a sandwich-type polyoxometalate

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Received: May 2011, Revised: June 2011, Accepted: July 2011

Abstract: Novel catalytic application of a sandwich-type polyoxometalate, $K_{12}[As_2W_{18}U_3O_{74}].21H_2O$, in synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes was investigated via three-component condensation reaction of b-naphthol and aromatic aldehydes. This method has the advantages of good yield, short reaction times and remarkable reusable activity of the catalyst. It was found that the best result was obtained when the reaction was carried out under solvent-free media and microwave irradiation.

Keywords: Synthesis, -naphthol, Aromatic aldehydes, 14-aryl-14H-dibenzo[a,j]xanthenes, Sandwich-type polyoxometalate, Catalyst

Introduction

Xanthenes and benzoxanthenes are biologically important drug intermediates. They are cited as active oxygen heterocycles possessing antibacterial and antiviral properties [1]. These compounds were obtained by the condensation reaction between -naphthol with aliphatic and aromatic aldehydes in the

presence of hydrochloric acid or phosphoric acid [2], sulfuric acid [3], p-toluenesulfonic acid [4], sulfamic acid [5], Amberlyst-15 [6], $HClO_4-SiO_2$ [7], Dowex-50W [8], $Yb(OTf)_3$ [9], alum [10] and Montmorillonite K-10 [11] as catalyst under different conditions. Many of these methods, however, suffer from longer reaction times, unsatis-

factory yields, harsh reaction conditions and excessive use of reagent and catalysts.

In this paper, we describe an efficient method for the condensation of aromatic aldehydes with b-naphthol to the corresponding 14-aryl-14H-dibenzo [a,j] xanthenes using catalytic amounts of sandwich-type polyoxometalate, $K_{12}[As_2W_{18}U_3O_{74}].21H_2O$ as novel recyclable catalyst under solvent-free condition by conventional heating and microwave irradiation.

Experimental

Materials and Apparatus

All chemical reagent were obtained from Merck and Romil, and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples by TLC, spectral and physical data. Melting points were determined on Electro-thermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Bruker Tensor 27 spectrometer with KBr pellet. The reaction was irradiated by using a microwave laboratory system of Milestone model. The purity of the substances and the progress of the reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel 60F containing the fluorescent indicator UV254.

General procedure for the synthesis of

14-aryl-14H-dibenzo[a,j]xanthenes in presence of catalysts by conventional heating program (Method A)

A mixture of an aldehyde (1 mmol), b-naphthol (2 mmol) and $K_{12}[As_2W_{18}U_3O_{74}].21H_2O$ (0.05 g, 0.008 mmol, 0.8 mol%) was heated at 125°C with stirring. After completion of reaction (monitored by TLC) the mixture was cooled and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 , and evaporated to give the crude product, which was recrystallized from ethanol to afford pure products.

General procedure for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes in presence of catalysts using microwave irradiation (Method B)

The experimental procedure for preparation of 14-aryl-14H-dibenzo[a,j]xanthenes by microwave irradiation was similar to conventional heating method with a application of microwave irradiation (900 W) for appropriate time.

Characterization of 14-aryl -14H-dibenzo[a,j]xanthenes 14-(3-nitrophenyl)-14H-dibenzo[a,j]xanthene (3a): mp: 210-211°C . IR (KBr, cm^{-1}): 3038, 2920, 1610, 1582, 1515, 1457, 1400, 1340, 1245, 1105, 964, 810, 800.

14-(2-chlorophenyl)-14H- dibenzo[a,j]xanthene (3b): mp: 214-216 °C. IR (KBr,

cm⁻¹): 3066, 2922, 1621, 1590, 1509, 1456, 1431, 1397, 1245, 1065, 959, 812, 775.

14-(2-hydroxyphenyl)-14H-dibenzo[a,j]xanthene (3c): mp: 127-128 °C. IR (KBr, cm⁻¹): 3393, 3058, 2928, 1628, 1596, 1514, 1464, 1437, 1404, 1257, 1188, 958, 818, 748.

Results and discussion

The catalyst plays a crucial role in the success of the reaction in terms of time and the yields. In the absence of the catalyst, the reaction of 3-nitrobenzaldehyde (1 mmol) with b-naphthol (2 mmol) as an example, could be carried out but the product was obtained in very low yield after prolonged time. We also studied the effect of the amount of the catalyst on this reaction. The use of 0.8 mol% of K₁₂[As₂W₁₈U₃O₇₄].21H₂O was sufficient to progress the reaction and an increase of the amount of catalyst did not improve the yield.

In continuation of our experiments, the condensation of 3-nitrobenzaldehyde and b-naphthol was performed in the presence of catalyst K₁₂[As₂W₁₈U₃O₇₄].21H₂O, un-

der different conditions. We found that the best result was obtained when the reaction was carried out under solvent-free media and microwave irradiation. After optimization of the reaction conditions, we studied the generality of these conditions to other substrates.

Using this method, different kinds of aromatic aldehydes and b-naphthol were heated in the presence of a catalytic amount of K₁₂[As₂W₁₈U₃O₇₄].21H₂O, the corresponding products were obtained in good yields. The results are summarized in Table 1. As shown in Table 1, the substituted functional groups on the aromatic ring of the aldehyde affected on the yield and reaction time. In comparison with electron with-drawing groups on the aryl aldehydes, we found that the presence of electron donating group on the aryl aldehyde decreased both the reaction rate and yield of product (Table 1, entry 3). In a typical experimental procedure, when reaction was complete, the catalyst was filtered, washed with ethyl acetate, dried at 70 °C for 1 h, and finally reloading the same catalyst for the new run without any appreciable loss of activity.

Table 1 Synthesis conditions of 14-aryl -14H-dibenzo[a,j]xanthenes using $K_{12}[As_2W_{18}U_3O_{74}].12H_2O$ under solvent-free conditions and microwave irradiation.

Entry	R	Product	Method A, Time (h)	Yield (%) ^a	Method B, Time (min)	Yield (%) ^a
1	3-NO ₂ C ₆ H ₅	3a	3.0	90	11	91
2	2-ClC ₆ H ₅	3b	2.5	87	10	86
3	2-OHC ₆ H ₅	3c	4.0	78	12	75

Method A: reaction carried out under conventional heating program in solvent-free conditions.

Method B: reaction carried out under microwave irradiation in solvent-free conditions.

^a Yields refer to pure products and all products were characterized from their spectral data and were compared with authentic samples.

References

- [1] Hideo, T; Chem. Abstr.; 95, 80922b; 1981.
- [2] Khorramabadi-zad, A. Kazemi, Z. Amiri Rudbari, H; J. Korean Chem. Soc.; 46, 541; 2002.
- [3] Sarma, R. J. Baruah, J. B; Dyes Pigment.; 64, 91; 2005.
- [4] Khorramabadi-Zad, A. Akbari, S. A. Shiri, A. Veisi, H; J. Chem. Res.; 277; 2005.
- [5] Rajitha, B. Kumar, B. S. Reddy, Y. T. Reddy, P. N. Sreenivasulu, N; Tetrahedron Lett.; 46, 8691; 2005.
- [6] Ko, S. Yao, C. F; Tetrahedron Lett.; 47: 8827; 2006.
- [7] Bigdeli, M. A. Heravi, M. M. Mahdavinia, G. H; J. Mol. Catal. A; 275, 25; 2007.
- [8] Shakibaei, G. I. Mirzaei, P. Bazgir, A; Appl. Catal. A; 325, 188; 2007.
- [9] Su, W. Yang, D. Jin, C. Zhang, B; Tetrahedron Lett.; 49, 3391; 2008.
- [10] Dabiri, M. Baghbanzadeh, M. Shakourinikcheh, M. Arzroomchilar, E; Bio Org. Med. Chem. Lett.; 18, 436; 2008.
- [11] Sharifi, A. Abae, S. Tavakoli, A. Mirzaei, M. Zolfaghareh, A; Synth. Commun.; 38, 2965; 2008.

کاربرد جدید کاتالیتیکی یک پلی اکسومتالات نوع ساندویچی

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دریافت: خرداد 1390، بازنگری: تیر 1390، پذیرش: شهریور 1390

چکیده: کاربرد جدید کاتالیستی یک پلی اکسومتالات نوع ساندویچی، $K_{12}[As_2W_{18}U_3O_{74}].21H_2O$ ، 14- آریل-14 H- [j,a] زانتنها، از طریق واکنش تراکمی سه جزئی β -نفتول و آلدیدهای آروماتیک بررسی شده است. این روش دارای مزایای بازده خوب، زمان واکنش کوتاه و فعالیت قابل توجه و مجدد کاتالیست است. بهترین نتیجه ها مربوط به حالتی است که واکنش در محیط بدون حلال و تابش ماکروویو انجام شده است

واژه های کلیدی: β -نفتول - آلدیدهای آروماتیک، 14- آریل-14 H [j,a] زانتنها، پلی اکسومتالات نوع ساندویچی، کاتالیست