

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

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To cite this article: Akbar Mobinikhaledi , Naser Foroughifar & Mohammad Ali Bodaghi Fard (2010) Eco-friendly and Efficient Synthesis of Pyrano[2,3-d] pyrimidinone and Tetrahydrobenzo[b]pyran Derivatives in Water, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:3, 179-185

To link to this article: <u>http://dx.doi.org/10.1080/15533171003629121</u>

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Eco-friendly and Efficient Synthesis of Pyrano[2,3-*d*] pyrimidinone and Tetrahydrobenzo[*b*]pyran Derivatives in Water

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Tetrahydrobenzo[b]pyran and pyrano[2,3-d]pyrimidinone derivatives were synthesized efficiently in the presence of KAl(SO₄)₂.12H₂O (alum) in water. Green media, lack of toxicity, short reaction times, easy work-up and high yields are some advantages of this method.

Keywords alum, green synthesis, heterogeneous, water

INTRODUCTION

The development of environmentally benign and clean synthetic procedures has become the goal of present day organic synthesis. Water plays an essential role in life processes and also as a medium for organic reactions.^[1,2] The organic reactions in aqueous media have attracted much attention in organic synthesis, not only because water is one of the most abundant, cheapest and environmentally friendly solvent, but also because water exhibits unique reactivity and selectivity, which is different and, in most cases, higher than those in conventional organic solvents.^[3] Reactions in aqueous media are environmentally safe, devoid of any carcinogenic effects, have a simple work up and especially are important in industry. Thus, there is a need for developing multicomponent reactions (MCRs) in water and without the use of any harmful organic solvents and catalysts. Tetrahydrobenzo[b]pyrans are an important class of heterocyclic scaffolds in the field of drugs and pharmaceutical. These compounds are widely used as anticoagulant, diuretic, spasmolytic, anticancer and antianaphylactic agents.^[4,5] Numerous methods have been reported for the synthesis of 4H-benzo[b]pyrans.^[6-15] However, some of these methods have drawbacks such as long reaction times, use of expensive reagents, low yields, harsh reaction conditions, effluent pollution and tedious work-up procedures. On the other hand, due to the diverse biological properties of pyranopyrimidinone derivatives, there is wide spread interest for their synthesis. Compounds with a uracil moiety have shown antitumor, antibacterial, antihypertensive, hepatoprotective, vasodilator, antiallergic, antifungal, antimalarial and herbicidal properties.^[16-19] There are several methods for the synthesis of pyranopyrimidinones under traditional thermal condition or microwave irradiation.^[20-23] Each of these reported methods has its own merits, with at least one of the limitation of drastic condition, long reaction times, low yields, and effluent pollution. KAl(SO₄)₂.12H₂O (alum) with mild acidity, involatility, and incorrositivity is insoluble in common organic solvents, and was used recently as an easily available acidic catalyst in different reactions.^[24-28] As a continuation of our research devoted to the development of green organic chemistry and one-pot multicomponent reactions (MCRs) for the synthesis of various heterocyclic compounds,^[29-32] herein we wish to report an efficient and green procedure for the preparation of 4*H*-benzo[*b*]pyrans and pyrano[2,3-*d*]pyrimidinones via a domino Knoevenagel-cyclocondensation reaction using $KAl(SO_4)_2.12H_2O$ (alum) as a catalyst in water.

EXPERIMENTAL

Melting points were measured by using capillary tubes on an electro thermal digital apparatus and are uncorrected. The progress of reactions was monitored by TLC using nhexane/EtOAc (2:1 v/v) as an eluent. IR spectra were recorded as KBr disc on a galaxy series FT-IR 5030 spectrometer. NMR spectra were recorded on a brucker spectrometer (300 MHz) in DMSO- d_6 with TMS as an internal standard. Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III).

Typical Procedures

General Procedure for Synthesis of Tetrahydrobenzo[b]pyrans

A mixture of an aromatic aldehyde (1 mmol), malononitrile(1 mmol), dimedone (1 mmol) and alum (10% mol) in water (5 ml) was heated at 80° C with stirring for appropriate time (see Table 1). After completion of the reaction confirmed by TLC, water (10–15 ml) was added and the reaction mixture

Received 10 October 2009; accepted 17 January 2010.

The authors would like to acknowledge financial support from the Research Council of Arak University.

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 TABLE 1

 Alum catalyzed synthesis of 4*H*-benzo[*b*]pyrans in water

Product	Ar	Time (min)	Yield (%) ^a	M.P (°C)	
				Found	Reported ^{Lit}
4a	C_6H_5	50	92	226-228	228-2306
4b	$4-Br-C_6H_4$	40	91	205-207	203-2057
4c	$3-Cl-C_6H_4$	45	90	227-229	$224 - 225^9$
4d	$4-Cl-C_6H_4$	40	93	212-214	209–211 ⁶
4e	$2,3-Cl_2-C_6H_3$	40	89	248-250	252-25414
4f	$2,4-Cl_2-C_6H_3$	45	93	182-184	180-18214
4g	$4-OH-C_6H_4$	40	90	204-207	206-20813
4h	$3-OH-C_6H_4$	45	92	231-233	236-23813
4i	$3-NO_2-C_6H_4$	40	90	210-212	212-214 ⁹
4j	$4-NO_2-C_6H_4$	45	92	179-181	$177 - 178^9$
4k	$2-NO_2-C_6H_4$	50	90	227-229	$224 - 226^9$
41	$4-CH_3-C_6H_4$	40	94	214-217	223-22513
4m	$4-N(Me)_2-C_6H_4$	40	92	222-225	230^{12}
4n	4-OCH ₃ -C ₆ H ₄	45	93	200–202	203 12

^aYields refer to isolated products.

cooled in a fridge to give the precipitate. The solid product was filtered and washed with cold water $(2 \times 10 \text{ ml})$. The pure product was obtained by recrystallization from ethanol:water (4:1).

General Procedure for Synthesis of Pyrano[2,3-d]pyrimidinones

A mixture of an aromatic aldehyde (1 mmol), malononitrile (1 mmol), barbituric acid (1 mmol) and alum (10% mol) in water (5 ml) was heated at 80°C with stirring for appropriate time (see Table 2). After completion of the reaction confirmed by TLC, water (10–15 ml) was added and the mixure cooled in a fridge to give the precipitate. The solid product was filtered and washed with cold water (2×10 ml). The pure product was obtained by recrystallization from ethanol:water (4:1).

Physical and Spectroscopic Data for Selected Compounds

(4a): IR (KBr) (ν_{max}): 3393, 3317, 3185, 2958, 2196, 1687, 1652, 1367 cm⁻¹. ¹H NMR (DMSO- d_6): δ H: 0.94 (3H, s, Me), 1.04 (3H, s, Me), 2.08 (1H, d, J = 16.0 Hz, H-6), 2.23 (1H, d, J = 16.0 Hz, H-6'), 2.50 (2H, m, CH₂), 4.11 (1H, s, H-4), 7.06 (2H, br s, NH₂), 7.19 (3H, m, H–Ar), 7.33 (2H, m, H–Ar). Anal. calcd for C₁₈H₁₈N₂O₂: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.97; H, 6.79; N, 9.42.

(4b): IR (KBr) (ν_{max}): 3398, 3319, 3211, 2966, 2191, 1683, 1656, 1369 cm⁻¹. ¹H NMR (DMSO- d_6): δ H: 0.97 (3H, s, Me), 1.06 (3H, s, Me), 2.12 (1H, d, J = 16.0 Hz, H-6), 2.28 (1H, d, J = 16.0 Hz, H-6'), 2.54 (2H, m, CH₂), 4.21 (1H, s, H-4), 7.13 (2H, br s, NH₂), 7.15 (2H, d, J = 8.5 Hz, H–Ar), 7.50 (2H, d, J = 8.5 Hz, H–Ar). Anal. calcd for C₁₈H₁₇BrN₂O₂:

Product	Ar	Time (min)	Yield (%) ^a	M.P (°C)	
				Found	Reported Lit
6a	4-Br-C ₆ H ₄	30	85	222–234	230-231 22
6b	3-Cl-C ₆ H ₄	35	80	243-245	240-24122
6c	$2,3-Cl_2-C_6H_3$	40	88	239-240	$240 - 242^{22}$
6d	$2,4-Cl_2-C_6H_3$	30	90	243-246	241-24222
6e	3-OH-C ₆ H ₄	35	87	161-163	158-160 ²²
6f	$3-NO_2-C_6H_4$	40	81	271-273	$268 - 270^{22}$
6g	$4-NO_2-C_6H_4$	35	80	236-238	$239 - 240^{22}$
6h	$4-CN-C_6H_4$	45	88	251-253	$254 - 256^{22}$

 TABLE 2

 Alum catalyzed synthesis of pyrano[2,3-d]pyrimidinones in water

^aYields refer to isolated products.



SCH. 1. Alum efficiently catalyzed the synthesis of pyrano[2,3-d]pyrimidinones and 4H-benzo[b]pyrans.

C, 57.92; H, 4.59; N, 7.51. Found: C, 58.17; H, 4.71; N, 7.43.

(4f): IR (KBr) (ν_{max}): 3533, 3364, 3153, 2966, 2193, 1685, 1658, 1367 cm⁻¹. ¹H NMR (DMSO- d_6): δ H: 1.00 (3H, s, Me), 1.06 (3H, s, Me), 2.11 (1H, d, J = 16.0 Hz, H-6), 2.27 (1H, d, J = 16.0 Hz, H-6'), 2.47–2.61 (2H, m, CH₂), 4.70 (1H, s, H-4), 7.15 (2H, br s, NH₂), 7.25 (1H, d, J = 8.4 Hz, H–Ar), 7.39 (1H, d, J = 8.4 Hz, H–Ar), 7.56 (1H, s, H–Ar). Anal. calcd for C₁₈H₁₆Cl₂N₂O₂: C, 59.52; H, 4.44; N, 7.71. Found: C, 59.91; H, 4.63; N, 7.63.

(4j): IR (KBr) (ν_{max}): 3394, 3323, 3213, 2970, 2193, 1683, 1655, 1523, 1365 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ H: 0.99 (3H, s, Me), 1.06 (3H, s, Me), 2.14 (1H, d, J = 16.0 Hz, H-6), 2.30 (1H, d, J = 16.0 Hz, H-6'), 2.53–2.57 (2H, m, CH₂), 4.39 (1H, s, H-4), 7.24 (2H, br s, NH₂), 7.48 (2H, d, J = 8.4 Hz, H–Ar), 8.21 (2H, d, J = 8.4 Hz, H–Ar). Anal. calcd for C₁₈H₁₇N₃O₄: C, 63.71; H, 5.05; N, 12.38. Found: C, 63.99; H, 5.17; N, 12.25. 4.4.5.

(4m): IR (KBr) (ν_{max}): 3381, 3321, 3209, 2962, 2191, 1682, 1656, 1367 cm⁻¹. ¹H NMR (DMSO- d_6): δ H: 0.97 (3H, s, Me), 1.06 (3H, s, Me), 2.10 (1H, d, J = 16.0 Hz, H-6), 2.27 (1H, d, J = 16.0 Hz, H-6'), 2.47–2.55 (2H, m, CH₂), 2.87 (6H, s, -N(Me)₂), 4.06 (1H, s, H-4), 6.66 (2H, d, J = 8.7 Hz, H–Ar), 6.95 (2H, br s, NH₂), 6.97 (2H, d, J = 8.7 Hz, H–Ar). Anal. calcd for C₂₀H₂₃N₃O₂: C, 71.19; H, 6.87; N, 12.45. Found: C, 71.49; H, 6.71; N, 12.33.

(6a): IR (KBr) (ν_{max}): 3391, 3302, 3188, 3072, 2197, 1718, 1674, 1408, 1280 cm⁻¹. ¹H NMR (DMSO-*d*₆): δ H: 4.26 (1H, s, H-5), 7.20 (2H, br s, NH₂), 7.22 (2H, d, J = 8.2 Hz, H–Ar), 6.51 (2H, d, J = 8.2 Hz, H–Ar) 11.12 (1H, br s, NH), 12.14 (1H, br s, NH). Anal. calcd for C₁₄H₉BrN₄O₃: C, 46.56; H, 2.51; N, 15.51. Found: C, 47.11; H, 2.63; N, 15.39. 4.4.7.

(6d): IR (KBr) (ν_{max}): 3389, 3305, 3184, 3078, 2193, 1718, 1676, 1410, 1282 cm⁻¹. ¹H NMR (DMSO–*d*₆): δ H: 4.75 (1H, s, H-5), 7.25 (2H, br s, NH₂), 7.38 (2H, s, H–Ar), 7.57 (1H, s, H–Ar), 11.13 (1H, br s, NH), 12.17 (1H, br s, NH). Anal. calcd for C₁₄H₈Cl₂N₄O₃: C, 47.89; H, 2.30; N, 15.96. Found: C, 47.72; H, 2.41; N, 15.85.

RESULTS AND DISCUSSION

To study the reaction in water, we tested the reaction of dimedone, malononitrile and 4-chlorobenzaldehyde in the presence of alum under different conditions. The best results were obtained with 10 mol% of alum at 80°C (93% yield). Encouraged by the above results, other 4*H*-benzo[*b*]pyran derivatives were synthesized in high yields under the same conditions (Scheme 1, Table 1).

We have also tested the reaction of barbituric acid, malononitrile and aromatic aldehyds in the presence of alum and observed that pyrano[2,3-d]pyrimidinone derivatives obtained in good yields (Scheme 1, Table 2).

The structure of products was confirmed by physical, spectroscopic (IR, ¹H NMR) and elemental analysis data. For example, scheme 2 and 3 show the ¹H- and ¹³C NMR spectra of **4f**, respectively. In the ¹H NMR spectrum of this compound (scheme 2) the broad singlet at $\delta = 7.15$ ppm is assigned to the resonance of the NH₂ group protons. The only proton of pyran ring appeared at $\delta = 4.70$ ppm. The signals related to the aromatic protons observed at $\delta = 7.23-7.56$ ppm. The other signals resonated at the expected regions. The ¹³C NMR spectrum of **4f** (scheme 3) shows 18 signals, which is also expected for this structure. The work-up of the reaction is accomplished by simple filtration (after cooling of the reaction mixture to room temperature and then below 5°C in a fridge), followed by



SCH. 2. ¹H NMR spectrum of 4f.

recrystalization from ethanol:water (4:1). These products are quite stable in aqueous media.

Although we have not established the mechanism of the reaction, a possible explanation is given in scheme 4. At the

first step, the olefin 8 is produced by a Knoevenagel condensation between the aryl aldehyde 1 and malononitrile 2 promoted by alum. The barbituric acid in the presence of alum could be converted to its corresponding barbiturate 9 that could



SCH. 3. ¹³C NMR spectrum of 4f.

easily react with olefin 8 to give the intermediate 10. The intermediate 10 converts to product 6 after proton transfer and tautomerization.

The role of water as the reaction medium and its mechanism is not clear. Despite the low solubility of starting materials in water, the reaction is accelerated in water and proceeds efficiently in the presence of alum. This one-pot reaction with regard to the reported observations^[3] may take place at the interface of organic substrates with water in a heterogeneous system. It is worthy to note that vigorous stirring is required for the success of this reaction.



SCH. 4. Proposed mechanism for one-pot synthesis of pyrano[2,3-d]pyrimidinones catalyzed by Alum in water.

CONCLUSION

In summary, we have developed an efficient method for the eco-compatible synthesis of 4H-benzo[b]pyrans and pyrano[2,3-d]pyrimidinone derivatives using a green media and catalyst. The easy purification of the products by simple filtration and recrystalization, neutral condition, high yields, short reaction times, the use of green and efficient catalyst and also the use of water as a solvent suggest good prospects for applicability of this process.

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