Research Article

Pentafluoropropionic Acid: An Efficient and Metal-Free Catalyst for the One-Pot Synthesis of Tetrahydrobenzo[*b*]pyran Derivatives

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Pentafluoropropionic acid (PFPA) efficiently catalyzes the one-pot, three-component reaction of aromatic aldehyde, malononitrile, and dimedone to yield tetrahydrobenzo[*b*]pyran derivatives in high yields. This method is of great value because of its easy processing, short reaction time, environmentally, and high yields.

1. Introduction

Tetrahydrobenzo[*b*]pyran derivatives are important classes of heterocyclic compounds. Tetrahydrobenzo[*b*]pyran compounds are known to possess a variety of biological activities, such as anticoagulant, spasmolytic, diuretic, anticancer, and antianaphylactin properties [1–5]. Furthermore these compounds can be employed as pigments, and they constitute the structural unit of a series of natural products [6, 7]. In view of different biological and chemical applications of tetrahydrobenzo[*b*]pyran derivatives, the development of suitable synthetic methodologies for generation has been a topic of great interest in recent times [8]. A number of 2-amino-tetrahydropyran derivatives are useful as photoactive materials [9]. Several methods have been reported for the synthesis of tetrahydrobenzo[*b*]pyran derivatives from aromatic aldehydes, dimedone, and malononitrile, involving the use of catalysts such as ZnO-beta zeolite [10], Mw-NaBr [11], Na₂SeO₄ [12], Caro's acide-SiO₂ [13], trisodium citrate [14], PPA-SiO₂ [15], KF-basic alumina under ultrasound irradiation [16], TEBA [17], 1-butyl-3-methylimidazolium hydroxide [18], sodium hypochlorite [19], 1,4-diazabicyclo[2.2.2]octane (DABCO) [20], triethylamine [21], Ce₁Mg_xZr_{1-x}O₂ [22], silica gel supported polyamine [23], urea-choline chloride [24], 2,2,2-trifluoroethanol [25], tetramethyl ammonium

hydroxide [26], ammonium acetate [27], and tetrabutylammonium bromide [28].

However, most of these procedures have significant drawbacks such as harsh reaction conditions, difficult workup, and expensive reagents. These problems promoted us towards further investigation in search for a new catalyst, which will carry out the synthesis of tetrahydrobenzo[*b*]pyrans under simpler experimental setup. In continuation of our efforts to develop novel synthetic routes using metal-free catalysts in organic reactions [29–31], and due to our interest in the synthesis of heterocyclic compounds [32], herein we wish to report an efficient synthesis of tetrahydrobenzo[*b*]pyran derivatives by cyclocondensation reaction of aromatic aldehydes, dimedone, and malononitrile using pentafluoropropionic acid as a metal-free catalyst (Scheme 1).

2. Experimental

2.1. General. All chemicals were obtained from Merck or Fluka and were used without further purification. Melting points were recorded on an electrothermal type 9100 melting point apparatus and are uncorrected. Infrared spectra were obtained in KBr disks on shimadzu IR-470 spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker,

TABLE 1: Optimizing the reaction conditions^a.

Entry	Catalyst (mol%)	Solvent	Condition	Time (min)	Yield (%) ^b
1	—	EtOH	Reflux	150	30
2	—	H ₂ O	Reflux	150	32
3	—	CHCl ₃	Reflux	180	25
4	—	CH ₃ CN	Reflux	150	28
5	—	EtOH : H ₂ O (1 : 1)	Reflux	120	34
6	—	EtOH	r.t	180	Trace
7	—	H ₂ O	r.t	180	Trace
8	—	CHCl ₃	r.t	180	Trace
9	—	CH ₃ CN	r.t	180	Trace
10	—	EtOH : H ₂ O (1 : 1)	r.t	180	Trace
11	(PFPA) 30	—	r.t	100	55
12	(PFPA) 35	—	r.t	100	66
13	(PFPA) 40	—	r.t	100	64
14	(PFPA) 30	EtOH : H ₂ O (1 : 1)	r.t	120	85
15	(PFPA) 35	EtOH : H ₂ O (1 : 1)	r.t	80	90
16	(PFPA) 40	EtOH : H ₂ O (1 : 1)	r.t	80	90
17	(PFPA) 35	EtOH	r.t	100	65
18	(PFPA) 35	H ₂ O	r.t	100	68
19	(PFPA) 35	CHCl ₃	r.t	120	47
20	(PFPA) 35	CH ₃ CN	r.t	100	56
21	(TFPA) 30	—	r.t	150	41
22	(TFPA) 35	—	r.t	150	52
23	(TFPA) 40	—	r.t	150	51
24	(TFPA) 30	EtOH : H ₂ O (1 : 1)	r.t	150	73
25	(TFPA) 35	EtOH : H ₂ O (1 : 1)	r.t	120	77
26	(TFPA) 40	EtOH : H ₂ O (1 : 1)	r.t	120	79
27	(TFPA) 35	EtOH	r.t	120	36
28	(TFPA) 35	H ₂ O	r.t	120	33
29	(TFPA) 35	CHCl ₃	r.t	180	24
30	(TFPA) 35	CH ₃ CN	r.t	120	29

^a Benzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1.2 mmol).^b Isolated yields.

SCHEME 1: Synthesis of tetrahydrobenzo[b]pyrans catalyzed by pentafluoropropionic acid.

DRX-400 Avance Bruker spectrometer, at 400.13 MHz and 100.22 MHz, respectively, in CDCl₃ and chemical shifts are in ppm (δ) relative to internal TMS.

2.2. General Procedure for the Synthesis of Tetrahydrobenzo[b]pyrans (4a-j). A solution of dimedone **1** (1 mmol), an aromatic aldehyde **2a-j** (1 mmol), malononitrile **3** (1.2 mmol), and pentafluoropropionic acid (35 mol%) in H₂O (10 mL) and EtOH (10 mL) was stirred at room temperature for the time

period as indicated in Table 1. The progress of the reaction was monitored by TLC. After completion of reaction, the solid product was collected by filtration and recrystallized from ethanol to afford pure products **4a-j** (Table 2) in high yields. All the products were identified by comparison of spectral data (IR and ¹H NMR) and m.p. with those reported.

2.3. Physical and Spectral Data for the Selected Compounds

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-benzopyran (4a). m.p. = 227–229°C; IR (KBr) cm⁻¹ 3410, 3330 (NH₂), 3050 (C–H), 2233 (CN), 1681 (C=O), 1380 (C–O); ¹H NMR (400.13 MHz, CDCl₃) δ (ppm): 7.32–7.19 (m, 5H), 4.56 (s, 2H, NH₂), 4.42 (s, 1H, CH), 2.47 (dd, 2H, *J* = 19.2 Hz, CH₂), 2.24 (dd, 2H, *J* = 16 Hz, CH₂), 1.13 (s, 3H, CH₃), 1.06 (s, 3H, CH₃).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-4H-benzopyran (4b). m.p. = 207–210°C; IR

TABLE 2: Synthesis of tetrahydrobenzo[*b*]pyrans using pentafluoropropionic acid as catalyst^a.

Entry	Ar	Product ^b	Time (min)	Yield (%) ^c	m.p., (°C) [reference]
1	C ₆ H ₅	4a	80	90	227–229 [28]
2	3-NO ₂ C ₆ H ₄	4b	80	89	207–210 [28]
3	4-MeOC ₆ H ₄	4c	60	90	197–199 [22]
4	4-MeC ₆ H ₄	4d	60	92	216–218 [13]
5	4-BrC ₆ H ₄	4e	60	90	206–208 [10]
6	3-MeOC ₆ H ₄	4f	80	90	207–209 [—]
7	3-ClC ₆ H ₄	4g	80	89	223–224 [13]
8	4-ClC ₆ H ₄	4h	60	92	213–215 [11]
9	2-ClC ₆ H ₄	4i	80	89	203–205 [14]
10	4-HOC ₆ H ₄	4j	80	90	206–208 [22]

^a Aromatic aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.2 mmol), and PFPA (35 mol%) in the mixture of EtOH : H₂O (1 : 1).^b The products were characterized by comparison of their spectroscopic and physical data with those reported in the literature.^c Isolated yield.TABLE 3: Comparison of efficiency of various catalysts in synthesis of tetrahydrobenzo[*b*]pyrans.

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Reference
1	Trisodium citrate	EtOH–H ₂ O; reflux	5–120	80–96	[14]
2	Na ₂ SeSO ₄	EtOH–H ₂ O; reflux	30–180	85–98	[12]
3	PPA–SiO ₂	H ₂ O; reflux	8–15	77–93	[15]
4	Caro's acid–SiO ₂	EtOH–H ₂ O; reflux	15–20	92–95	[13]
5	ZnO–beta zeolite	EtOH; reflux	35–52	86–95	[10]
6	NaBr	MW; 70–80 °C	10–15	85–95	[11]
7	TBAB	EtOH; reflux	20–140	87–95	[28]
8	NaOCl	Grinding	10–30	80–88	[19]
9	Ce ₁ Mg _x Zr _{1–x} O ₂	EtOH; reflux	35–45	90–94	[22]
10	Supported polyamine	EtOH–H ₂ O; reflux	120–220	88–95	[23]
11	Urea–ChCl	80 °C	60–240	75–95	[24]
12	TMAH	H ₂ O; r.t.	30–120	80–92	[26]
13	PFPA	EtOH–H ₂ O; r.t.	60–80	89–92	This work

(KBr) cm^{−1} 3420, 3300 (NH₂), 3012 (C–H), 2257 (CN), 1710 (C=O), 1557, 1360 (NO₂); ¹H NMR (400.13 MHz, CDCl₃) δ (ppm): 8.11–7.48 (m, 4H), 4.80 (s, 2H, NH₂), 4.53 (s, 1H, CH), 2.50 (dd, *J* = 13.2 Hz, 2H, CH₂), 2.25 (dd, *J* = 16 Hz, 2H, CH₂), 1.12 (s, 3H, CH₃), 1.08 (s, 3H, CH₃).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-4H-benzopyran (4d). m.p. = 216–218 °C; IR (KBr) cm^{−1} 3421, 3297 (NH₂), 2966 (C–H), 2194 (CN), 1674 (C=O), 1369 (C–O); ¹H NMR (400.13 MHz, CDCl₃) δ (ppm): 7.08–7.14 (m, 4H), 4.54 (s, 2H, NH₂), 4.38 (s, 1H, CH), 2.46 (dd, *J* = 5.2 Hz, 2H, CH₂), 2.29 (s, 3H, CH₃), 2.23 (dd, *J* = 5.6 Hz, 2H, CH₂), 1.12 (s, 3H, CH₃), 1.06 (s, 3H, CH₃).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3-methoxyphenyl)-5-oxo-4H-benzopyran (4f). m.p. = 207–209 °C; IR (KBr) cm^{−1} 3397, 3291 (NH₂), 2295 (CN), 1678 (C=O), 1384 (C–O); ¹H NMR (400.13 MHz, CDCl₃) δ (ppm): 7.29–6.76 (m, 4H), 4.57 (s, 2H, NH₂), 4.40 (s, 1H, CH), 3.81 (m, 3H, CH₃), 2.47 (dd, *J* = 19.6 Hz, 2H, CH₂), 2.26 (dd, *J* = 18 Hz, 2H, CH₂), 1.14 (s, 3H, CH₃), 1.08 (s, 3H, CH₃); ¹³C NMR (100.22 MHz, CDCl₃) δ (ppm): 27.7 (CH₃), 28.8

(CH₃), 32.2 (C), 35.4 (CH₂), 40.6 (CH₂), 50.6 (CH₃), 55.2 (CH), 63.5 (C), 112.3 (CH), 113.5 (CH), 113.9 (C), 118.6 (C), 119.9 (CH), 129.6 (CH), 144.8 (C), 157.4 (C), 159.7 (C), 161.6 (C), 195.8 (C).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4-chlorophenyl)-5-oxo-4H-benzopyran (4h). m.p. = 213–215 °C; IR (KBr) cm^{−1} 3421, 3105 (NH₂), 2185 (CN), 1686 (C=O), 1356 (C–O); ¹H NMR (400.13 MHz, CDCl₃) δ (ppm): 7.25–7.02 (m, 4H), 4.57 (s, 2H, NH₂), 4.41 (s, 1H, CH), 2.47 (s, 2H, CH₂), 2.24 (dd, *J* = 16.4 Hz, 2H, CH₂), 1.14 (s, 3H, CH₃), 1.05 (s, 3H, CH₃).

3. Result and Discussion

In order to optimize the reaction conditions, including solvents and temperature, the reaction was conducted under various conditions and the results are listed in Table 1. In an optimized reaction condition, benzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1.2 mmol) in H₂O (10 mL) and EtOH (10 mL) were mixed in the presence of

pentafluoropropionic acid (35 mol%) as catalyst for 60–80 min. The reaction proceeds very cleanly at room temperature and was free of side products. After completion of the reaction (monitored by TLC), a simple workup affords the products in high yields (Scheme 1). Among the solvents tested, the reaction in H₂O, EtOH, CHCl₃, and CH₃CN using 35 mol% of the catalyst gave a moderate yield of the desired product at room temperature. However in the mixture of EtOH and H₂O relatively high yield of the product is obtained at room temperature after 80 min. Without catalyst, in refluxing EtOH, H₂O, CHCl₃, CH₃CN, and mixture of EtOH-H₂O or at room temperature in these solvents the reaction times are prolonged and the yields are poor. In the solvent-free conditions, even in the presence of 40 mol% of the catalyst at room temperature, the yields are moderate. The results are summarized in Table 1. For comparison, we also investigated the efficiency of trifluoroacetic acid (TFAA) as catalyst in this model reaction. As shown in Table 1, it can be seen that PFPFA proved to be a better catalyst than TFAA in terms of reaction time and yield.

We also evaluated the amount of pentafluoropropionic acid required for this transformation. It was found that the yield of product was affected by the catalyst amount. Increasing the amount of the catalyst up to 35 mol% in the mixture of EtOH and H₂O at room temperature increased the yield of the product. Further increase in the catalyst amount did not increase the yield noticeably. In order to show generality and scope of this new protocol, we used various substituted aromatic aldehydes and the results obtained are summarized in Table 2.

In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the expected products in high yields and short reaction times. The type of aldehyde had no significant effect on the reaction. The efficiency of pentafluoropropionic acid as a catalyst for the synthesis of the 2-amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-benzopyran (**4a**), was compared with that of other catalysts reported in the literature. Some of the results are summarized in Table 3. It is clear from this table that pentafluoropropionic acid is an efficient and environmentally benign catalyst which could be useful in the synthesis of a series of tetrahydrobenzo[*b*]pyran derivatives.

4. Conclusion

In conclusion, a mild and efficient method is proposed for the one-pot three-component reactions of aromatic aldehydes, dimedone, and malononitrile using pentafluoropropionic acid catalyst for synthesis of tetrahydrobenzo[*b*]pyran derivatives. Some attractive features of this protocol are high yields, easy workup, and the simplicity of the procedure.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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