

## Hydroxy sodalite zeolite as a recyclable catalyst for the green synthesis of tetrahydrobenzo[*b*]pyrans via one-pot three-component condensation reaction

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### ABSTRACT

The utilization of hydroxy sodalite (H-SOD) as catalyst under solvent-free condition is described for the efficient preparation of tetrahydrobenzo[*b*]pyrans. These compounds are synthesized by three-component reactions of aldehydes, alkyl nitriles and dimedone. H-SOD that is the waste-product of zeolite manufacturing process is used as an efficient and a very inexpensive catalyst. Furthermore, it can be reused for several rounds without significant loss of activity. The key features of this reported protocol are neutral conditions, excellent yields, short reaction time, simple work-up and recovery and reusability of catalyst. Small E-factor and large percent of reaction mass efficiency, which are very useful metrics for industry, are advantages of this environmentally benign process.

**Keywords:** Hydroxy sodalite, Tetrahydrobenzo[*b*]pyran, Aldehyde, Dimedone.

### 1. Introduction

H-SOD is a compact and stable kind of aluminosilicate (zeolite) that sometimes is produced as unwanted and undesirable product in zeolite 4A plants. Usually, in zeolite manufacturing plants, this product directed to the pool of chemical wastes. High alkalinity of H-SOD and the risk of spreading in the groundwater is an issue that always threatens the environment [1]. In this way, applying H-SOD as a useful compound, is imperative and can act as an active field of environmental research. H-SOD is used as water adsorbing agent in purification of water/1,1-dimethylhydrazine mixture [2] and dehydrating agent in conversion of alcohols to ethers or alkenes [3]. In this paper, we study the use of H-SOD as an efficient catalyst for synthesis of tetrahydrobenzo[*b*]pyrans via one-pot three component condensation reaction (Scheme 1).

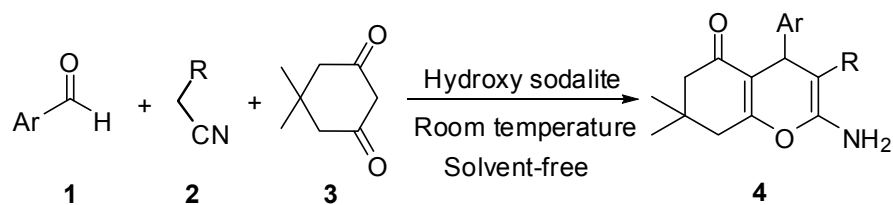
Tetrahydrobenzo[*b*]pyrans exhibit interesting biological and pharmacological activities such as anti-coagulant [4], anti-cancer [5], anti-anaphylactic [6], spasmolytic [7] and diuretic [8]. Furthermore, these compounds can act as pigments [9] and photoactive materials [10].

Considering the importance of these compounds, many methods have been employed for the synthesis of 5-oxo-5,6,7,8-tetrahydrobenzo[*b*]pyran derivatives.

The conventional reported syntheses involve the condensation of dimedone with aromatic aldehyde and malononitrile under reflux in acetic acid [11] or DMF [12]. Other methods include the use of tetrabutyl ammonium bromide [13], tetramethyl ammonium hydroxide [14], (*S*)-proline [15], rare earth perfluorooctanoates [16], amino-functionalized ionic liquid [17], sodium selenate [18], sodium bromide [19], KF-alumina [20] and so on under classical heating, microwave or ultrasonic irradiation. Each of the above methods have the following drawbacks such as, using expensive and toxic solvents, strong acidic conditions, long reaction times, low yields, tedious work-up, harsh reaction condition and reacting at high temperature. Due to these problems and wide range applications of tetrahydrobenzo[*b*]pyrans, development of an easy, new and efficient catalyst with high catalytic activity, short reaction time, recyclability and simple workup for the preparation of these compounds under neutral, mild and practical conditions is of prime interest.

There is an increasing interest in the use of environmentally feasible reagents particularly in

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R = CN, CO<sub>2</sub>Et, CO<sub>2</sub>Me

**Scheme 1.** Synthesis of tetrahydrobenzo[*b*]pyrans.

solvent-free conditions. Prevention of organic solvents during reactions in organic synthesis leads to a clean, efficient, and economical technology; not only with the increment of safety, the simpleness of work up and the reduction of cost, but also increased amounts of reactants can be achieved in the same equipment without huge modifications. Reactivity and sometimes selectivity may be enhanced without dilution [21].

## 2. Experimental

### 2.1. Materials

The chemical used in this work were purchased from Fluka (Buchs, Switzerland) and Merck. Also, H-SOD which is used as catalyst in this work was obtained from Nokan Process Company. The XRF analysis of H-SOD was determined with Magix-Pro and XRD spectrum of it was measured with Bruker D4 Endeavor.

All products were characterized by comparison of their physical and spectroscopic data with those of authentic samples. Melting points were measured on the Buchi B-545 apparatus and are uncorrected. IR spectra were measured on a Pu 9624, Philips FT-IR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured with a Bruker Ultrasheild spectrometer at 500.1 and 125.8 MHz using TMS as internal standard.

### 2.2. General procedure

A mixture of aromatic aldehyde (**1**, 1 mmol), alkyl nitrile (**2**, 1 mmol) dimeredone (**3**, 1 mmol, 140 mg) and H-SOD (0.5 g) in test tube was stirred at room temperature for an appropriate time (Table 5). After completion of the reaction confirmed by TLC, the mixture was extracted from ethanol (2×5 ml), then the solvent evaporated in vacuum and the obtained solid compound was collected.

### Selected spectral data

#### (4a):

IR (KBr):  $\bar{\nu}$  = 3390, 3256, 2883, 2133, 1630 cm<sup>-1</sup>. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.21-7.34 (5H, m, H-Ar), 4.54 (2H, brs, NH<sub>2</sub>), 4.44 (1H, s, CH), 2.49 (2H, brs, CH<sub>2</sub>), 2.28 (1H, d, *J* = 16.3 Hz, CH), 2.23 (1H, d, *J* = 16.3 Hz, CH), 1.14 (3H, s, CH<sub>3</sub>), 1.07 (3H, s, CH<sub>3</sub>)

ppm. <sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 196.2, 162.1, 158.5, 134.5, 128.8, 127.8, 127.2, 124.5, 119.5, 114.3, 51.0, 40.1, 36.0, 32.5, 29.2, 27.9 ppm.

#### (4b):

IR (KBr):  $\bar{\nu}$  = 3391, 3249, 2882, 2130, 1628 cm<sup>-1</sup>. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.14-7.34 (4H, m, H-Ar), 5.54 (2H, brs, NH<sub>2</sub>), 4.18 (1H, s, CH), 2.54 (2H, brs, CH<sub>2</sub>), 2.23 (1H, d, *J* = 16.1 Hz, CH), 2.14 (1H, d, *J* = 16.1 Hz, CH), 1.01 (3H, s, CH<sub>3</sub>), 0.93 (3H, s, CH<sub>3</sub>) ppm.

#### (4d):

IR (KBr):  $\bar{\nu}$  = 3391, 3253, 2883, 2131, 1641 cm<sup>-1</sup>. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.31-7.58 (4H, m, H-Ar), 4.61 (2H, brs, NH<sub>2</sub>), 4.34 (1H, s, CH), 2.50 (2H, brs, CH<sub>2</sub>), 2.23 (1H, d, *J* = 16.0 Hz, CH), 2.12 (1H, d, *J* = 16.0 Hz, CH), 1.06 (3H, s, CH<sub>3</sub>), 0.97 (3H, s, CH<sub>3</sub>) ppm.

#### (4g):

IR (KBr):  $\bar{\nu}$  = 3381, 3336, 2967, 2881, 2153, 1680 cm<sup>-1</sup>. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.63-7.06 (4H, m, H-Ar), 5.88 (1H, s, OH), 5.63 (2H, brs, NH<sub>2</sub>), 4.10 (1H, s, CH), 2.47 (2H, brs, CH<sub>2</sub>), 2.25 (1H, d, *J* = 16.0 Hz, CH), 2.06 (1H, d, *J* = 16.0 Hz, CH), 1.03 (3H, s, CH<sub>3</sub>), 0.94 (3H, s, CH<sub>3</sub>) ppm.

#### (4i):

IR (KBr):  $\bar{\nu}$  = 3374, 3132, 2881, 2131, 1628 cm<sup>-1</sup>. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.21-7.34 (4H, m, H-Ar), 4.54 (2H, brs, NH<sub>2</sub>), 4.44 (1H, s, CH), 2.73 (6H, s, CH<sub>3</sub>), 2.29 (2H, brs, CH<sub>2</sub>), 2.07 (1H, d, *J* = 16.2 Hz, CH), 2.02 (1H, d, *J* = 16.2 Hz, CH), 1.14 (3H, s, CH<sub>3</sub>), 1.07 (3H, s, CH<sub>3</sub>) ppm. <sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 196.3, 158.4, 152.5, 146.6, 138.7, 136.2, 129.1, 120.0, 113.3, 51.0, 41.1, 40.3, 40.8, 35.0, 32.4, 29.2, 28.0 ppm.

## 3. Results and discussion

In connection with our previous work on solid state organic transformations [22] we wish to report a green, simple and environmentally benign methodology for the synthesis of 5-oxo-5,6,7,8-tetrahydro benzo[*b*]pyrans using H-SOD as a very inexpensive, eco-friendly and easily available catalyst under neutral

and solvent-free conditions. This method not only affords the products in excellent yields but also avoids the problems associated with catalyst cost, handling, safety and pollution. Also, the reaction time is relatively shortened in the presence of this heterogeneous catalyst.

Table 1 shows the XRF analysis of H-SOD and the XRD spectra in Fig. 1. confirm its crystallinity. In a typical experimental procedure, firstly, equimolar amount of benzaldehyde (**1a**), malononitrile (**2a**) and dimedone (5,5-dimethyl-1,3-cyclohexadione) (**3**), were chosen as the model reaction to detect whether the use of H-SOD was efficient and to investigate the optimized conditions. The results are summarized in Table 2. In the absence of H-SOD the desired 2-amino-7,7- dimethyl-5- oxo-4- phenyl- 5, 6, 7, 8- tetrahydro benzo[*b*]pyran (**4a**) was not obtained and no reaction would take place even at high temperature (Table 2, entries 1 and 2). On the other hand, **4a** could be obtained in the presence of a catalytic amount of H-SOD, but the product yield was still not satisfactory (Table 2, entry 3). Further studies showed that an increase in the dosage of H-SOD improved the reaction yield significantly. We changed the amount of catalyst from 0.25 g to 1.0 g and found that 0.5 g was good enough to obtain satisfactory yields (Table 2, entries 3-6). As shown in Table 2, the yield could not be

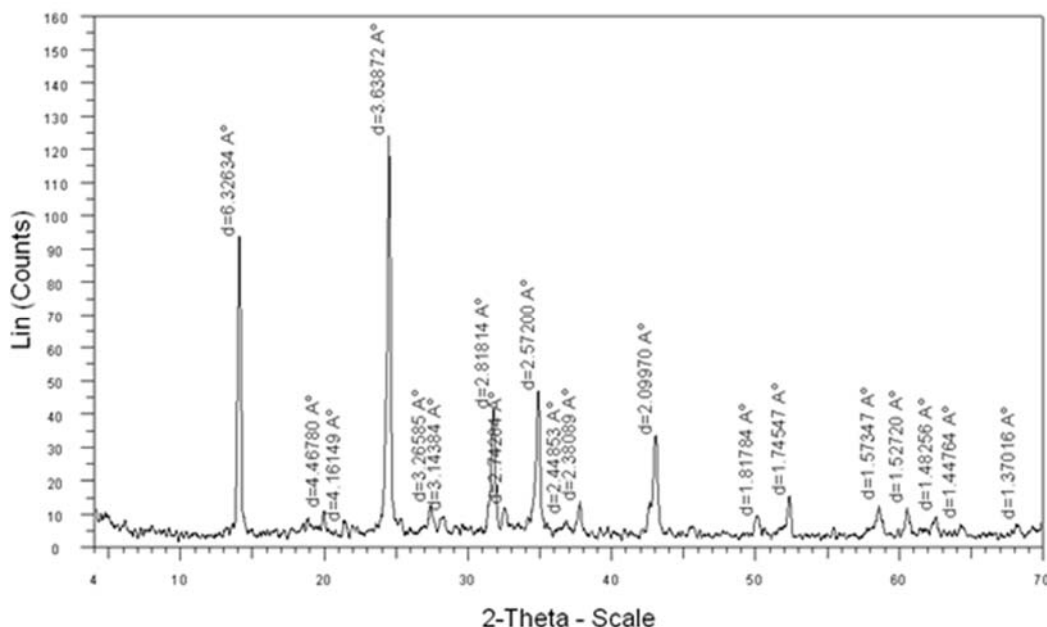
improved further when the amount of H-SOD exceeded. In order to investigate the reusability of catalyst, the catalyst was extracted from the reaction mixture and reloaded with fresh reagent for future runs after reactivation (100°C at oven for 24 h). No considerable decrease in the yield was observed, demonstrating that H-SOD can be reused as a catalyst in one-pot synthesis of tetrahydrobenzo[*b*]pyrans. In view of green chemistry, recovery and reusability of the catalyst is highly preferable.

Having established the advantages of H-SOD as catalyst, bearing in mind that solvents can also effect the chemical reaction, we continued to optimize the process by varying the solvents. EtOH, toluene, THF and etc. (shown in Table 3), were chosen as the medium for comparison. In each case, **1a** (1 mmol), **2a** (1 mmol) and **3** (1 mmol) were mixed together with H-SOD (0.5 g) and solvent (10 mL) under reflux conditions. Also, we examined the reaction without solvent by heating at 70°C. From the results obtained, it clears that solvent-free conditions at room temperature and heating (70°C) gave the highest yields of the desired product **4a**. When the organic solvents were used, the reaction was not complete even after refluxing for several hours and in addition, some unidentified by-products were detected. In the case of heating (70°C) under solvent-free condition, the yield

**Table 1.** XRF analysis of H-SOD.

Species	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SO <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	LOI <sup>a</sup>
Content (W%)	32.08	27.07	21.92	0.27	0.17	<0.10	<0.10	18.54

<sup>a</sup> Loss on ignition



**Fig. 1.** X-ray diffractogram of H-SOD.

**Table 2.** Synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydrobenzo[*b*]pyran (4a): Effect of catalyst.<sup>a</sup>

Entry	H-SOD (g)	Time (h)	Yield (%) <sup>b</sup>
1	0	24	-
2	0	24	4 <sup>c</sup>
3	0.25	3	65
4	0.5	3	96
5	0.75	3	96
6	1.0	3	96
7	0.5 <sup>d</sup>	3	96, 94, 91, 91

<sup>a</sup>Room temperature under solvent-free conditions.<sup>b</sup>Isolated yield.<sup>c</sup>Heating (90°C) under solvent-free condition.<sup>d</sup>Catalyst was reused four times.

of the product was similar to ambient temperature condition. Thus, it is clear that carrying out the reaction at room temperature in the presence of catalytic amount of H-SOD without any solvent is the best condition.

The greenness of a process is determined by many factors and E-factor and reaction mass efficiency are important ones that are defined as [23]:

$$\text{E-factor} = \frac{\text{total waste (kg)}}{\text{product (kg)}}$$

$$\text{Reaction mass efficiency(\%)} = 100 \times \frac{\text{Mass of product(Kg)}}{\text{Summation of the masses of the reactant that remains in the product(Kg)}}$$

Here, these metrics are calculated and Table 4 shows the comparison of these two parameters between our method and the other reports. The results clearly show that carrying out the reaction at room temperature in the presence of catalytic amount of H-SOD without any solvent is better than the other systems.

Reaction time and yield are the two parameters that determine the efficiency of a catalyst. These features and the similar ones in other studies are summarized in Table 5 for H-SOD catalyst. The synthesis yield for 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydrobenzo[*b*]pyran (**4a**) catalyzed with H-SOD in comparison with the other methods is good and the reaction time due to its condition (solvent free, room temperature) is ideal.

Based on the results obtained above, we apply the methodology to several other derivatives (Table 6) and

**Table 3.** Synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydrobenzo[*b*]pyran (**4a**): Effect of solvents.<sup>a</sup>

Entry	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	Ethanol	4	55
2	Ethylacetate	4	57
3	Toluene	5	12
4	Cyclohexane	8	10
5	THF	5	29
6	Water	4	50
7	None <sup>c</sup>	3	96

<sup>a</sup>Refluxed for the time given.<sup>b</sup>Isolated yield.<sup>c</sup>Heating (70°C) under solvent-free condition.

**Table 4.** Comparison of green chemistry factors between H-SOD and other catalyst.

Entry	Catalyst	E-factor <sup>a</sup>	Reaction mass efficiency (%)	Ref.
1	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NBr	111.8	86.54	[13]
2	(CH <sub>3</sub> ) <sub>4</sub> NOH	201.2	68.26	[14]
3	[RE(PFO) <sub>3</sub> ]	69.31	84.81	[16]
4	Na <sub>2</sub> SeO <sub>4</sub>	65.53	91.35	[18]
5	NaBr	32.63	89.42	[19]
6	KF-Alumina	43.05	80.10	[20]
7	H-SOD	30.60	90.38	This work

<sup>a</sup>The content of extraction and recrystallization solvents was not reported in the references, thus these solvent contents are measured experimentally.

found that in all cases, the reaction proceeded rapidly to afford the corresponding 2-amino-7,7-dimethyl-5-oxo-4-aryl-5,6,7,8-tetrahydrobenzo [*b*] pyran derivatives. All the yields were excellent and it seems that the effect of substituted groups on the aromatic aldehydes is not very strong; both electron-donating and electron-withdrawing groups worked well, showing little distinction.

A mechanism for the formation of 2-amino-7,7-dimethyl-5-oxo-4-aryl-5,6,7,8-tetrahydrobenzo [*b*] pyran derivatives (**4a-4m**) can be explained by the tentative mechanism presented in Scheme 2. Initially, aldehyde (**1**) and activated alkyl nitrile (**2**) with H-SOD, react each other via Knoevenagel condensation to give the compound (**A**), then **A** reacts with activated dimedone (**3**) to give the intermediate (**B**) which produce **4** via cyclization.

#### 4. Conclusions

In summary, we found a green method for the synthesis of tetrahydrobenzo[*b*]pyran derivatives by the three-component reactions of aldehydes, alkyl nitriles and dimedone under solvent-free conditions. The features of this procedure are mild reaction conditions, high yields, operational simplicity and the environmentally friendly method. Meanwhile, H-SOD that is the waste-product of zeolite manufacturing process is used as an efficient, excellent, readily available reagent and a very inexpensive catalyst. Furthermore, it can be reused for several rounds without significant loss of activity.

#### Acknowledgements

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**Table 5.** Comparison the catalyst efficiency between H-SOD and other catalyst.

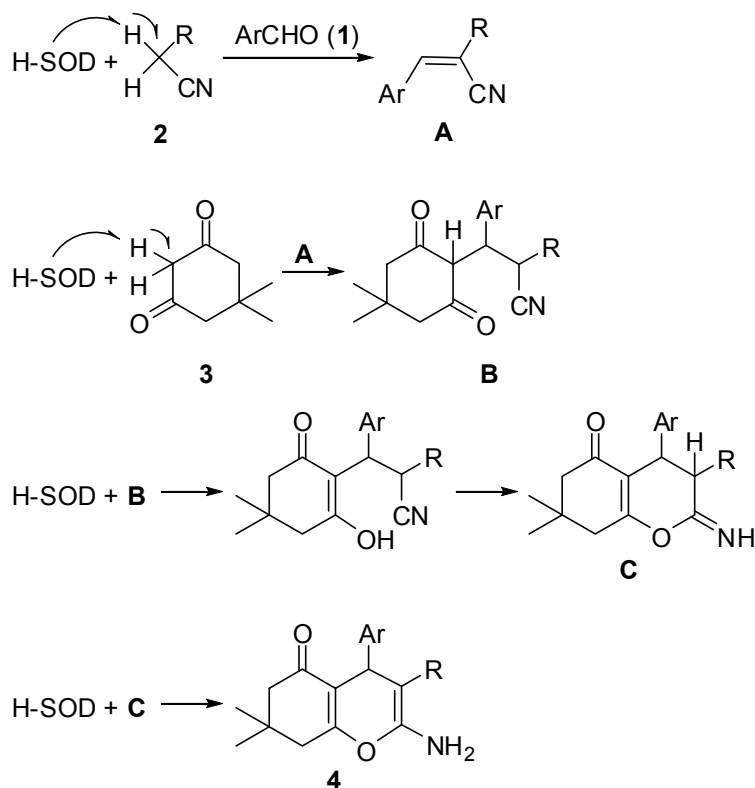
Entry	Catalyst	Yield (%)	Reaction time	Reaction condition	Ref.
1	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NBr	92/ 88/ 94	5-7 (min)	EtOH/ H <sub>2</sub> O/ Grinding <sup>a</sup> (Reflux)	[13]
2	(CH <sub>3</sub> ) <sub>4</sub> NOH	81	0.5-2 (h)	H <sub>2</sub> O/ Room temperature	[14]
3	[RE(PFO) <sub>3</sub> ]	90	5 (h)	EtOH/ 60°C	[16]
4	Na <sub>2</sub> SeO <sub>4</sub>	97	1 (h)	EtOH: H <sub>2</sub> O/ Reflux	[18]
5	NaBr	95	10 (min)	Microwave irradiation (70°C)	[19]
6	KF-Alumina	85	14-20 (h)	Grinding/ Room temperature	[20]
7	H-SOD	96	3 (h)	Room temperature	This work

<sup>a</sup>This reaction is carried in three different reflux conditions.

**Table 6.** H-SOD catalyzed synthesis of 4*H*-benzo[*b*]pyrans (**4a-4m**) at room temperature under solvent-free conditions (Scheme 1).

Entry	Ar	R	Time (h)	Yield (%) <sup>a</sup>	m.p. (°C)		Ref.
					Found	Reported	
<b>a</b>	C <sub>6</sub> H <sub>5</sub>	CN	3	96	228-230	226-228	[11]
<b>b</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	4	97	208-211	208-210	[15]
<b>c</b>	3-Cl-C <sub>6</sub> H <sub>4</sub>	CN	4	91	223-226	224-225	[13]
<b>d</b>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CN	4	88	177-179	177-178	[16]
<b>e</b>	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CN	4	93	209-210	208-211	[16]
<b>f</b>	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	CN	3	92	215-217	214-216	[24]
<b>g</b>	4-OH-C <sub>6</sub> H <sub>4</sub>	CN	3	89	205-207	206-208	[16]
<b>h</b>	3-OH-C <sub>6</sub> H <sub>4</sub>	CN	3	89	230-234	231-233	[14]
<b>i</b>	4-(CH <sub>3</sub> ) <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	CN	3	90	200-203	202-204	[16]
<b>j</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	4	95	149-151	150-152	[11]
<b>k</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Me	4	94	166-169	167-168	[11]
<b>l</b>	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	4	90	179-183	182-184	[25]
<b>m</b>	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Me	4	91	189-191	190-192	[25]

<sup>a</sup>Yields refer to those of pure isolated products characterized by IR, <sup>1</sup>HNMR and <sup>13</sup>CNMR spectroscopic data.

**Scheme 2.** Mechanism for the formation of tetrahydrobenzo[*b*]pyrans.

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