Tetrahedron 69 (2013) 6399-6403

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Palladium-catalyzed hydrogenation with use of ionic liquid bis(2-hydroxyethyl)ammonium formate [BHEA][HCO₂] as a solvent and hydrogen source^{\dagger}



Tetrahedron

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ARTICLE INFO

Article history: Received 4 March 2013 Received in revised form 20 May 2013 Accepted 23 May 2013 Available online 28 May 2013

Keywords: Ionic liquids Hydrogenation Aromatic ketones Nonflammability Reuse

ABSTRACT

We designed ionic liquid bis(2-hydroxyethyl)ammonium formate [BHEA][HCO₂] for use as a solvent and hydrogen donor for hydrogenation. Catalytic hydrogenation of aromatic ketones, nitro groups, and olefins with PdCl₂ in [BHEA][HCO₂] generated the corresponding reduction products. Selective reduction of aromatic ketones over aliphatic ketones was observed. Hydrogenolysis of benzyl ethers and benzyl amines also proceeded. All these reactions were successfully carried out in good to excellent yields under mild and nonflammable conditions. In addition, the ionic liquid and Pd source can be reused several times. © 2013 Elsevier Ltd. All rights reserved.

1. Introduction

lonic liquids are a new class of materials that have been extensively studied since the last decade.^{2,3} Ionic liquids have attracted increasing interest due to their unique properties, such as negligible volatility, high thermal stability, low toxicity, and reusability, which in turn makes them prominent candidates to replace conventional organic solvents. Current research on ionic liquids has shown that they support a large and diverse range of organic reactions, such as Heck reaction,⁴ Suzuki cross-coupling reaction,⁶ Sonogashira–Hagihara reaction,⁶ Negishi cross-coupling reaction.⁷

The typical method for the synthesis of alcohols by hydrogenation of aromatic ketones using Pd and H₂ is widely employed even now because of the convenient experimental procedures and/or because green reactions can be carried out.^{8–16} However, problems related to flammability and reusability are encountered in the method. While reduction with Pd and ammonium formate is well known, there are only few examples of its application in the reduction of aromatic ketones.^{17,18} We reasoned that the problems of hydrogenation using Pd/C with H_2 could be overcome if the ionic liquid is used both as a solvent and as a reagent. That is, an ionic liquid that contains a formate counter anion should serve as a hydrogen source (Fig. 1).



Fig. 1. Hydrogenation in ionic liquid with formate ions.



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^{0040-4020/\$ —} see front matter \odot 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2013.05.103

Herein, we report the results of hydrogenation of various substrates, including aromatic ketones, with a Pd source in an ionic liquid.

2. Results and discussion

Acetophenone (**1**) was selected as the substrate in order to afford 1-phenylethanol (**2**) by hydrogenation using Pd/C with H₂ (Table 1, entry 5). Ionic liquids containing formate and 2-hydroxyethylammonium moiety were selected as the solvent and reagent to facilitate convenient extraction of the product after the reaction (Fig. 2).^{6,19–21}

Table 1

Screening of ionic liquids

	O II	PdCl ₂ (10 mol%) ionic liquid (40 eq.)	ОН	
	Ph Me	r.t., 2 h	Ph Me	
	1		2	
Entry	Ion	ic liquid	Yield ^a (%)	
			2	1
1	[HE	A][HCO ₂]	2 57	1 21
1 2	(HE (HE	A][HCO ₂] PA][HCO ₂]	2 57 73	1 21 19
1 2 3	[HE [HE [BH	A][HCO ₂] PA][HCO ₂] EA][HCO ₂]	2 57 73 81	1 21 19 5
1 2 3 4	(HE (HE (BH (DE	A][HCO ₂] PA][HCO ₂] EA][HCO ₂] HEA][HCO ₂]	2 57 73 81 20	1 21 19 5 56

^a Isolated yield.

 $^b\,$ Reaction was carried out with 10 wt % Pd/C (ca. 5 mol % of Pd metal) and H_2 in MeOH.

 $\begin{array}{c} \mathsf{HCO}_2^{\ominus} \\ \mathsf{HO} \\ & \stackrel{\mathsf{I}}{\overset{\mathsf{I}}{\oplus}} \\ \mathsf{HO} \\ & \stackrel{\mathsf{I}}{\overset{\mathsf{I}}{\oplus}} \\ & \mathsf{R}^2 \end{array} \xrightarrow{[\mathsf{HEA}][\mathsf{HCO}_2] : \mathsf{R}^1 = \mathsf{H}, \mathsf{R}^2 = \mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_3} \\ & [\mathsf{HEPA}][\mathsf{HCO}_2] : \mathsf{R}^1 = \mathsf{H}, \mathsf{R}^2 = \mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH} \\ & [\mathsf{BHEA}][\mathsf{HCO}_2] : \mathsf{R}^1 = \mathsf{H}, \mathsf{R}^2 = \mathsf{CH}_2\mathsf{CH}_2\mathsf{OH} \\ & [\mathsf{DEHEA}][\mathsf{HCO}_2] : \mathsf{R}^1 = \mathsf{R}^2 = \mathsf{CH}_2\mathsf{CH}_3 \end{array}$

Fig. 2. Selected ionic liquids.

Reactions of **1** with $PdCl_2$ (10 mol %) for 2 h at rt in four types of ionic liquids produced **2** in various yields. Ionic liquids [HEPA] [HCO₂] and [BHEA][HCO₂] containing secondary ammonium ions afforded **2** in higher yields compared to [HEA][HCO₂] and [DEHEA][HCO₂] (Table 1). The advantage in these reactions is the use of stable Pd^{II} as the Pd source. Based on this result, we decided to use [BHEA][HCO₂] as the model ionic liquid for further research.

The quantity of $PdCl_2$ to afford a hydrogenation product in good yield within a practical period should be more than 10 mol % (Table 2, entries 1–4). Although we attempted this reaction using various Pd sources, no other Pd source was found to give higher yield than PdCl₂ did (Table 2, entries 3 and 5–8).

The reductive ability of ketones in this method was strongly dependent on the solubility of the substrate and the electronic character of the substituent. Addition of the co-solvent (DMF) to the ionic liquid system involving a solid substrate made the yield increase (Table 3, entries 4-8 and 11). Ketones adjoining a benzene ring that contained an electron donating group at the *ortho* or *para* position afforded the reductive product in poor yield (Table 3, entries 1, 3, 4, and 8). On the other hand, ketones

Table 2

Table 2

Effects of the quantity, temperature, and type of Pd source on yield

	O F I [BHEA][HC	Pd [BHEA][HCO ₂] (40 eq.)		
	Ph´ Me r 1	.t.	Ph´ Me 2	
Entry	Pd	Time (h)	Yield ^a (%)	
			2	1
1	PdCl ₂ (1 mol %)	24	12	76
2	PdCl ₂ (5 mol %)	24	68	26
3	PdCl ₂ (10 mol %)	2	83 (81)	13 (5)
4	PdCl ₂ (20 mol %)	2	99	1
5	Pd(OAc)2 (10 mol %)	2	5	78
6	Pd(OCOCF ₃) ₂ (10 mol %)	2	7	85
7	Pd(NO ₃) ₂ (10 mol %)	2	16	64
8	PdSO ₄ (10 mol %)	2	26	63

^a Determined by ¹H NMR analysis of the crude reaction mixture; isolated yields are shown in parentheses.

Reaction of various ketones					
D ¹		PdCl ₂ (20 [BHEA][HCC	0 mol%) 0 ₂] (40 eq.)		
R	₹ 3a-I	r.t		R	4a-I
Entry	R ¹	R ²		Time (h)	Yield ^a (%)
1	o-Me	Me	3a	24	8
2	<i>m</i> -Me	Me	3b	24	85
3	<i>p</i> -Me	Me	3c	24	40
4 ^b	<i>p</i> -OMe	Me	3d	24	10
5 ^b	p-CF ₃	Me	3e	2	94 (91)
6 ^D	p-CO ₂ Me	Me	3f	0.25	96 (96)
7 ⁰	Н	Ph	3g	24	76 (76)
8 ^b		Me	3h	24	9
9		O Me	3i	8	92 (95)
10		0	3j	24	67
11 ^b	Ph	Ph	3k	24	88 (88)
12	Ph	O Me	31	72	0

 $^{\rm a}$ Determined by $^1{\rm H}$ NMR analysis of the crude reaction mixture; isolated yields are shown in parentheses.

^b Reactions were carried out with DMF (5 mL) as the co-solvent.

adjoining a benzene ring that contained an electron withdrawing group afforded the corresponding alcohol in excellent yield within a short span of reaction time (Table 3, entries 5 and 6). Although the reduction of aryl ketone proceeded, dialkyl ketone did not produce the corresponding alcohol (Table 3, entries 11 and 12). These findings were applied to the selective reduction among carbonyl groups, which cannot occur by the conventional method (with H_2 and Pd/C) and by NaBH₄ reduction (Scheme 1).

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Scheme 1. Selective hydrogenation.

Next, we investigated the scope of this reaction. Hydrogenation of nitrobenzene (**9**), *trans*-stilbene (**11a**), *cis*-stilbene (**11b**), and diphenylacetylene (**13**) proceeded in excellent yields (Table 4, entry 1–4). The aniline (**10**) was converted into acetanilide (**22**) for the low boiling point. The dehalogenation of aryl halides proceeded in good yields (Table 4, entries 5 and 6). The deprotection of the aromatic amines and aromatic alcohols with a Cbz or a benzyl protecting group proceeded in good to excellent yields (Table 4, entries 7–9). However, the deprotection of aliphatic alcohols with a benzyl protecting group did not proceed (Table 4, entry 10). Further, extraction of aliphatic amines from the ionic liquid [BHEA][HCO₂] was difficult.

Table 4

Reactions	corresponding	to va	rious	substrates
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Entry	Substrate	Product	PdCl ₂ (mol %)	Time (h)	Yield ^b (%)
1	<u> </u>	10	1	12	96 ^c
2 ^d	Ph 11a	Ph 12	5	24	95
3	Ph Ph 11b	Ph Ph 12	5	24	94 ^e
4 ^d	Ph-=-Ph 13	Ph 12	5	24	98 ^e
5	CI OH	OH 15	20	24	81 ^e
6	OH Br	OH 15	20	4	90
7	NHCbz 16	NH ₂ 10	1	24	97 ^c
8	NHBn 17	✓ NH ₂ 10	5	24	76 ^c
9 ^d	OBn 18	OH 19	10	12	93
10	Ph Me 20	Ph Me 21	20	168	0

^a Reactions were carried out using PdCl₂ and [BHEA][HCO₂] at rt.

^b Isolated yield.

^d Reactions were carried out with DMF (5 mL) as the co-solvent.

^e Determined by ¹H NMR analysis of the crude reaction mixture.

We then explored the reusability of the ionic liquid in hydrogenation of **1** to **2** (Table 5). The reusability of Pd and [BHEA][HCO₂] was tested without the addition of formic acid. Although the reaction time was extended in order to obtain a yield higher than 70%, the product was successfully obtained even in the fifth cycle of the reaction. Recycling experiments were also attempted by adding formic acid to the collected ionic liquid containing Pd. However, the results in terms of yield and reaction time were not as remarkable as those in the case of the reuse.

Table 5

Experiment on reusability of acetophenone (1)

	o ⊥	PdCl ₂ (20 mol%) [BHEA][HCO ₂]	OH 人
	Ph´ `Me 1	r.t.	Ph `Me 2
Cycle		Time	Yield ^a (%)
1		2 h	93
2		6 h	96
3		36 h	70
4		6 d	77
5		18 d	73
6		92 d	22 ^b

^a Determined by ¹H NMR analysis of the crude reaction mixture.
 ^b Isolated yield.

Additional reusability experiments were conducted using nitrobenzene (**9**), *trans*-stilbene (**11a**), and *cis*-stilbene (**11b**) as the substrate (Tables 6–8). Until the fifth cycle, good yields were obtained when using **9** as the substrate (Table 6). The reaction time was extended as in the case of **1**. When **11a** and **11b** were utilized as substrates, the reaction proceeded in good yield until up to the third cycle (Tables 7 and 8). Even when the co-solvent DMF was used, the reusability experiments were successful.

Table 6

Experiment on reusability of nitrobenzene (9)



1	1	87
2	4	86
3	8	81
4	16	84
5	65	84

 $^{\rm a}\,$ The two-step yield: aniline (10) was converted into a cetanilide (22). $^{\rm b}\,$ Isolated yield.

Table 7

Experiment on reusability of trans-stilbene (11a)

	N Ph	PdCl ₂ (20 mol%) [BHEA][HCO ₂], DMF	∽ Ph	
	Ph 💛 '''	>	Ph / / / /	
	11a	1.t.	12	
Cycle		Time [h]		Yield % ^a
1		2		90
2		12		90
3		24		92
4		72		68

^a Determined by ¹H NMR analysis of the crude reaction mixture.

^c The two-step yield: aniline (10) was converted into acetanilide (22).

Experiment on reusability of <i>cis</i> -stilbene (11b)			
	PdCl ₂ (20 mol%) [BHEA][HCO ₂], DMF		
Ph´ Ph 11b	r.t.	Pł	

11b		12
Cycle	Time (h)	Yield ^a (%)
1	2	91
2	12	99
3	24	95
4	72	68

^a Determined by ¹H NMR analysis of the crude reaction mixture.

Furthermore, this reaction solution did not ignite even when PdCl₂ was introduced in the middle of the reaction under a condition that would have certainly caused the ignition of the reaction solution in the case of Pd/C with H₂. Thus, a new nonflammable hydrogenation system with ionic liquid and catalyst was established.

3. Conclusion

We developed a new hydrogenation system using ionic liquids. This method is more useful in terms of flammability and reusability than the conventional method (with H_2 and Pd/C). Since this method has advantages in terms of the solvent, reagent, and catalyst, it is certainly superior to the conventional system. In addition, selective reduction of aromatic ketones over aliphatic ketones was observed when this method was employed.

4. Experimental section

4.1. General

IR spectra were recorded on a JASCO FT/IR 350 spectrometer. ¹H NMR and ¹³C NMR spectra were run on a Varian NMR System 600, or a JEOL AL-300 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm), and the signals are described as s (singlet), d (doublet), t (triplet), q (quartet), br (broad), and m (multiple). Coupling constants (*J* values) are given in Hertz. Merck silica gel 60 (230–400 mesh) was employed for column chromatography.

Compounds $2,^{22}$ 4a, 22 4b, 23 4c, 22 4d, 22 4e, 24 4f, 25 4g, 26 4h, 27 4i, 28 4j, 22 4k, 29 6, 30 7, 31 8, 32 12, 33 15, 34 19, 21, 22 35 are all known compounds. These compounds were identified by comparing the spectral data with an authentic sample or a commercially available.

4.2. Preparation of ionic liquids

[HEA][HCO₂], [HEPA][HCO₂], [BHEA][HCO₂], and [DEHEA] [HCO₂] were prepared by dropping the stoichiometric amount of formic acid to corresponding amino alcohol at 0 °C. The reaction mixture was stirred at rt for 2 h under argon atmosphere. After completion of the reaction, the ionic liquid was washed with EtOAc and Et₂O. The ionic liquid was dried in vacuo at 40 °C.

4.3. Typical experimental procedure

(Table 2, entry 3): To a solution of acetophenone (1) (120 mg, 1.00 mmol) in [BHEA][HCO₂] (5.00 mL, 39.7 mmol) was added PdCl₂ (17.7 mg, 10.0 mol %) at rt and the reaction mixture was stirred at the same temperature for 2 h under argon atmosphere. The mixture was poured into brine (10 mL) and extracted with EtOAc (10×10 mL). The organic layer was washed with brine (150 mL) and dried with MgSO₄. After removal of the solvent, the residue was subjected to column chromatography (Merck Kieselgel 60,

 ϕ =2.0 cm, *l*=13.0 cm; EtOAc-hexane, 1:5) to give 1-phenylethanol (**2**) as colorless oil; yield: 99.5 mg (81%).

(Table 3, entry 5): To a solution of 4'-(trifluoromethyl)acetophenone (**3e**) (188 mg, 1.00 mmol) in DMF (5.00 mL) was added [BHEA][HCO₂] (5.00 mL, 39.7 mmol) and PdCl₂ (35.5 mg, 20.0 mol %) at rt and the reaction mixture was stirred at the same temperature for 2 h under argon atmosphere. The mixture was poured into brine (10 mL) and extracted with Et₂O (10×10 mL). The organic layer was washed with brine (150 mL) and dried with MgSO₄. After removal of the solvent, the residue was subjected to column chromatography (Merck Kieselgel 60, ϕ =2.0 cm, *l*=7.5 cm; EtOAc-hexane, 1:5) to give 1-(4-trifluoromethylphenyl)ethanol (**4e**) as colorless oil; yield: 174 mg (91%).

(Scheme 1): To a solution of 1-phenyl-1,4-pentanedione (**5**) (176 mg, 1.00 mmol) in [BHEA][HCO₂] (5.00 mL, 39.7 mmol) was added PdCl₂ (17.7 mg, 10.0 mol %) at rt and the reaction mixture was stirred at the same temperature for 24 h under argon atmosphere. The mixture was poured into brine (10 mL) and extracted with EtOAc (10×10 mL). The organic layer was washed with brine (100 mL) and dried with MgSO₄. After removal of the solvent, the residue was subjected to column chromatography (Merck Kieselgel 60, ϕ =2.0 cm, *l*=24.0 cm; EtOAc–hexane, 1:3) to give 5-hydroxy-5-phenylpentane-2-one (**6**) as colorless oil; yield: 152.9 mg (86%).

(Scheme 1): To a solution of 1-phenyl-1,4-pentanedione (**5**) (176 mg, 1.00 mmol) in MeOH (5.00 mL) was added 10 wt % Pd/C (53.2 mg) at rt and the reaction mixture was stirred at the same temperature for 24 h under H₂ atmosphere. After filtration and removal of the solvent, the residue was subjected to column chromatography (Merck Kieselgel 60, ϕ =2.0 cm, *l*=20.0 cm; EtOAc-hexane, 1:20) to give 5-phenyl-2-pentanone (**7**) as colorless oil; yield: 120.6 mg (74%).

(Scheme 1): To a solution of 1-phenyl-1,4-pentanedione (**5**) (176 mg, 1.00 mmol) in MeOH (5.00 mL) was added NaBH₄ (83.2 mg, 2.20 mmol) at rt and the reaction mixture was stirred at the same temperature for 30 min under argon atmosphere. The mixture was poured into H₂O (5 mL) and extracted with EtOAc (3×10 mL). The organic layer was washed with brine (30 mL) and dried with MgSO₄. After removal of the solvent, the residue was subjected to column chromatography (Merck Kieselgel 60, ϕ =2.0 cm, *l*=13.0 cm; EtOAc—hexane, 1:3) to give 1-phenyl-1,4-pentanediol (**8**) as colorless oil; yield: 175.6 mg (97%).

(Table 4, entry 1): To a solution of nitrobenzene (**9**) (123 mg, 1.00 mmol) in [BHEA][HCO₂] (5.00 mL, 39.7 mmol) was added PdCl₂ (1.80 mg, 1.00 mol %) at rt and the reaction mixture was stirred at the same temperature for 12 h under argon atmosphere. The mixture was poured into brine (10 mL) and extracted with EtOAc (10×10 mL). The organic layer was washed with brine (150 mL) and dried with MgSO₄. To a solution was added acetic anhydride (2.84 mL, 30 mmol) at rt and the reaction mixture was stirred at the same temperature for 30 min under argon atmosphere. The mixture was washed with a saturated solution of sodium carbonate (80 mL), brine (150 mL), and dried with MgSO₄. After removal of the solvent, the residue was subjected to column chromatography (Merck Kieselgel 60, ϕ =2.0 cm, *l*=11.5 cm; EtOAc–hexane, 1:3) to give acetanilide (**22**); yield: 130 mg (96%).

4.4. Typical experimental procedure for the reuse experiments

(Table 5): To a solution of acetophenone (1) (120 mg, 1.00 mmol) in [BHEA][HCO₂] (5.00 mL, 39.7 mmol) was added PdCl₂ (35.5 mg, 20.0 mol %) at rt and the reaction mixture was stirred at the same temperature for 2 h under argon atmosphere. The mixture was extracted with Et_2O (20×10 mL). The organic layer was washed with brine (200 mL) and dried with MgSO₄. The solvent was removed under reduced pressure to give crude reaction mixture.

Yield was directly determined by ¹H NMR spectroscopy. The remaining [BHEA][HCO₂] was used in the next reaction without further purification.

4.5. 2-Hydroxyethylammonium formate [HEA][HCO₂]

Colorless liquid; ¹H NMR (600 MHz, DMSO- d_6): δ 8.41 (s, 1H, CHO), 7.09 (br s, 4H, NH, and OH), 3.54 (t, *J*=5.4 Hz, 2H, CH₂CH₂OH), 2.79 (t, *J*=5.4 Hz, 2H, CH₂CH₂OH); ¹³C NMR (150 MHz, DMSO- d_6): δ 167.3, 58.1, 41.5; IR (neat): 3360, 2370, 1575, 1350, 1070, 1015, 770 cm⁻¹

4.6. 2-Hydroxyethylpropylammonium formate [HEPA][HCO₂]

Colorless liquid; ¹H NMR (600 MHz, DMSO- d_6): δ 8.37 (s, 1H, CHO), 3.59 (t, *J*=5.4 Hz, 2H, CH₂CH₂OH), 2.85 (t, *J*=5.4 Hz, 2H, CH₂CH₂OH), 2.74 (t, *J*=7.2 Hz, 2H, CH₂CH₂CH₃), 1.57 (qt, *J*=7.2, 7.2 Hz, 2H, CH₂CH₂CH₃), 0.88 (t, *J*=7.2 Hz, CH₃); ¹³C NMR (150 MHz, DMSO- d_6): δ 167.0, 56.9, 49.2, 48.6, 19.2, 11.1; IR (neat): 3365, 2970, 2830, 1595, 1365, 1080, 775 cm⁻¹

4.7. Bis(2-hydroxyethyl) ammonium formate [BHEA][HCO₂]

Colorless liquid; ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.35 (s, 1H, CHO), 6.33 (br s, 4H, NH, and OH), 3.59 (t, *J*=5.4 Hz, 4H, CH₂CH₂OH), 2.87 (t, *J*=5.4 Hz, 4H, CH₂CH₂OH); ¹³C NMR (150 MHz, DMSO-*d*₆): δ 167.3, 56.9, 49.4; IR (neat): 3330, 2830, 1590, 1450, 1350, 1070, 945, 775 cm⁻¹

4.8. Diethyl(2-hydroxyethyl) ammonium formate [DEHEA] [HCO₂]

Colorless liquid; ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.30 (s, 1H, CHO), 3.59 (t, *J*=6.0 Hz, 2H, CH₂CH₂OH), 2.85 (q, *J*=7.2 Hz, 4H, *CH*₂CH₃), 2.83 (t, *J*=6.0 Hz, 2H, *CH*₂CH₂OH), 1.08 (t, *J*=7.2 Hz, 6H, CH₂CH₃); ¹³C NMR (150 MHz, DMSO-*d*₆): δ 166.6, 56.1, 53.4, 46.7, 8.8; IR (neat): 3340, 2980, 2830, 2680, 1600, 1475, 1365, 1080, 775 cm⁻¹

Acknowledgements

We are grateful to the SC-NMR Laboratory of Okayama University for the use of the facilities.

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