

Available online at www.sciencedirect.com



Tetrahedron

Tetrahedron 62 (2006) 3985-3988

Temperature-controlled highly selective dimerization of α-methylstyrene catalyzed by Brönsted acidic ionic liquid under solvent-free conditions

Haiming Wang, Peng Cui, Gang Zou, Fan Yang and Jie Tang*

Department of Chemistry, East China Normal University, 3663 North Zhongshan Rd., Shanghai 200062, China

Received 21 November 2005; revised 10 February 2006; accepted 10 February 2006

Available online 7 March 2006

Abstract—A temperature-controlled highly selective dimerization of α -methylstyrene to produce 2,4-diphenyl-4-methyl-1-pentene and 1,1,3-trimethyl-3-phenylindan was catalyzed by Brönsted acidic ionic liquid [Hmim]⁺BF₄⁻. At 60 °C, 2,4-diphenyl-4-methyl-1-pentene was formed in 93% selectivity with >92% conversion under a solvent-free condition while 1,1,3-trimethyl-3-phenylindan could be obtained in 100% selectivity when the reaction temperature was increased to 170 °C. The ionic liquid [Hmim]⁺BF₄⁻ could be reused with almost no loss of activity.

© 2006 Elsevier Ltd. All rights reserved.

1. Introduction

Brönsted acid-catalyzed dimerization of α -methylstyrene (AMS) generally produces a mixture of three isomers: 2,4-diphenyl-4-methyl-1-pentene (1-PT), 2,4-diphenyl-4-methyl-2-pentene (2-PT) and the saturated cyclic isomer, 1,1,3-trimethyl-3-phenylindan (Indan) (Scheme 1).¹



Scheme 1. Brönsted acid-catalyzed dimerization of α -methylstyrene.

Among the dimers, 2,4-diphenyl-4-methyl-1-pentene (1-PT) is a versatile molecular weight regulator that is odorless and has few effects on the color and stability of resulting polymers, thus widely used in polymerization

producing polystyrene, ABS resin and the likes.¹ The saturated cyclic isomer, 1,1,3-trimethyl-3-phenylindan (Indan), also has wide applications in polymers, for example, as a photo and thermo stabilizer,² plasticizer³ as well as mobility and viscosity modifier⁴ in the production of polystyrene or ABS resin. The Brönsted acid-catalyzed dimerization of AMS is the straightest way to produce these useful chemicals.¹ However, due to the interconvertion and the difficulties of separation of these isomers, highly selective dimerization of AMS is the precondition for practical process for production of the desired isomers, especially for the production of 1-PT. The acidity of Brönsted acid catalysts and reaction temperature have proved to be crucial to the selectivity in the dimerization of AMS.

Ionic liquids, featuring low volatility as well as high thermal and chemical stability, have attracted much attention as environmentally friendly replacement for traditional volatile organic solvents in catalysis and organic transformations.⁵ Brönsted acidic ionic liquids have been recently reported to serve as both reaction medium and catalysts in many organic transformations.⁶ A sulfonic acid based Brönsted acidic ionic liquid, *N*-alkyl-N'-(4-sulfonic butyl) imidazolium triflate, was reported to catalyze dimerization of AMS under solvent-free conditions.⁷ However, a mixture of 1-PT, 2-PT and Indan was generated with poor selectivity. We have recently described a highly selective dimerization of *a*-methylstyrene for 1-PT in a Brönsted acidic ionic liquid, [Hmim]⁺BF₄⁻, where [Hmim]⁺BF₄⁻ severed as both catalyst and reaction medium.⁸ Herein, we further report a temperature-controlled dimerization of

Keywords: Brönsted acidic ionic liquid; α-Methylstyrene; Dimerization.

^{*} Corresponding author. Tel.: +86 21 62232764; fax: +86 21 62232100; e-mail: jtang@chem.ecnu.edu.cn

^{0040–4020/\$ -} see front matter @ 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2006.02.025

AMS for highly selective production of 1-PT and Indan catalyzed by $[Hmim]^+BF_4^-$ under solvent-free conditions.

2. Results and discussion

2.1. Effects of the loading of $[\text{Hmim}]^+\text{BF}_4^-$ on the dimerization

Although $[Hmim]^+BF_4^-$ represents the simplest and the most readily prepared ionic liquid, it would be attractive, especially in practical respect, to use the ammonium in minimum amount in the dimerization of AMS, for example, as catalyst, if the high selectivity for 1-PT could be maintained. To our delight, when $[\text{Hmim}]^+\text{BF}_4^-$ previously used as solvent was reduced to 50 mol% of AMS the selectivity for 1-PT and rate of the dimerization of AMS just slightly decreased within experimental errors at 60 °C. Further investigations showed the selectivity in the dimerization of AMS was not sensitive to the loading of the Brönsted acidic ionic liquids (Table 1). For example, when the molar ratio of $[\text{Hmim}]^+\text{BF}_4^-$ to AMS was reduced from 4/1, 1/1 to 1/2, the selectivity for 1-PT decreased from 93.5, 91.2 to 90.3% and with conversion of AMS reaching 96.4, 93.1 and 93.5%, respectively, in 10 h (Table 1, entries 1, 3 and 6). In fact, further reducing the loading of $[\text{Hmim}]^+\text{BF}_4^-$ to 25 mol% of AMS slightly increased the selectivity of 1-PT (92.8%) while the rate of dimerization decreased sharply and only 23.9% AMS was converted after 10 h. Interestingly, the selectivity of 1-PT, 2-PT and Indan remained almost unchanged at low conversion of AMS (Table 1, entries 8–10).

Table 1. [Hmim]⁺BF₄⁻ promoted dimerization of AMS at 60 °C

Entry	IL/AMS	Time (h)	Conv. (%)	Distribution of dimers (%) ^a		
				Indan	1-PT	2-PT
1	4/1	10	96.4	0.5	93.5	6.0
2	1/1	5	90.0	2.7	91.5	5.8
3	1/1	10	93.1	2.9	91.2	5.9
4	1/1	24	98.1	4.0	89.1	6.9
5	1/2	5	69.5	3.0	91.5	5.5
6	1/2	10	93.5	3.4	90.3	6.3
7	1/2	24	94.7	3.5	90.1	6.4
8	1/4	5	13.8	1.6	93.0	5.4
9	1/4	10	23.9	1.8	92.8	5.4
10	1/4	24	49.2	2.1	92.2	5.7

^a Determined by GC.

2.2. Recycling of the ionic liquid $[Hmim]^+BF_4^-$

Separation of $[\text{Hmim}]^+\text{BF}_4^-$ from the organics is very simple. Organic layer was readily separated from the ionic liquid by decanting and the residue was washed by hexane and dried in vacuum to recycle the ionic liquid $[\text{Hmim}]^+\text{BF}_4^-$. Due to the gel-like property, about 5–10% weight of $[\text{Hmim}]^+\text{BF}_4^-$ was lost for each cycle. Thus for each reuse, some (5–10% weight) fresh $[\text{Hmim}]^+\text{BF}_4^-$ was added to keep the constant weight of the ionic liquid for each experiment. Since the dimerization was very slow at low loading of $[\text{Hmim}]^+\text{BF}_4^-$ it reasonable to omit the influence of the newly added ionic liquid on the dimerization. The reuse of catalytic system was investigated with $[\text{Hmim}]^+\text{BF}_4^-/\text{AMS}=1:2$ (mol/mol) at 60 °C and results were collected in Table 2. As revealed in Table 2, the dimerization showed almost no change with respect to conversion and selectivity.

Table 2.	Recycling	[Hmim]	BF_4	in the	dimerization	of	AMS
----------	-----------	--------	--------	--------	--------------	----	-----

Recycle	Conv. (%) ^b	Indan	1-PT	2-PT	
1	95	3.5	90.1	6.4	
2	96	4.5	89.5	6.1	
3	95	4.4	90.3	5.3	
4	93	3.9	90.2	5.9	
5	96	4.1	90.5	5.4	
6	95	4.3	89.6	6.1	

^a Reaction was carried out at 60 °C for 24 h with $[\text{Hmim}]^+\text{BF}_4^-/\text{AMS}=1:2$ (mol/mol).

^b Determined by GC.

2.3. Effects of temperature on the dimerization

The reaction temperature showed a great effect on both the selectivity and the rate of dimerization of AMS catalyzed by 25 mol% [Hmim] $^+BF_4^-$ (Table 3). The conversion of AMS decreased from 92.5 to 78.4% for 48 h as reaction temperature being lowered from 60 to 40 °C (Table 3, entries 1 and 2). Further elongating the reaction time did not increase the AMS conversion remarkably at 60 °C, implying that the reaction could be very slow at low concentration of AMS. However, when the reaction was conducted at 80 °C the conversion reached 92.7% in 24 h, just half of that at 60 °C (Table 1, entry 10), but the 1-PT selectivity decreased to 86.9% (Table 3, entry 6). No AMS was detected by GC after 10 and 5 h when the reaction was carried out at 120 and 150 °C, respectively (Table 3, entries 8 and 9). However, the selectivity of the dimerization was poor and cyclic isomer, Indan, became the major product in the later case (Table 3, entries 9 and 10).

Table 3. Temperature effects on the $[Hmim]^+BF_4^-$ catalyzed dimerization of AMS^a

Entry	<i>T</i> (°C)	Time (h)	Conv. (%)	Distribution of dimers (%) ^b		
				Indan	1-PT	2-PT
1	40	48	78.4	1.8	93.4	4.8
2	60	48	92.5	2.2	92.6	5.2
3	60	90	92.7	2.5	92.1	5.4
4	80	5	44.8	4.2	89.1	6.7
5	80	10	64.4	4.4	88.4	7.2
6	80	24	92.7	5.8	86.9	7.3
7	120	5	98.0	37.0	48.5	14.5
8	120	10	100	43.5	39.5	17.0
9	150	5	100	62.0	24.5	13.5
10	150	10	100	76.5	9.5	13.0

^a Reaction was carried out with $[Hmim]^{+}BF_{4}^{-}/AMS = 1:4 \text{ (mol/mol)}.$ ^b Determined by GC.

According to the mechanism of acid-catalyzed dimerization of AMS, Indan was formed from ionic dimeric intermediate, which could be formed not only from dimerization of AMS but also from 1-PT and 2-PT under acidic conditions (Scheme 2).

Therefore, we anticipated, using the same catalyst system, it should be possible to convert the chain isomers 1-PT and 2-PT into cyclic isomer Indan, for which most acid-catalyzed

3987



Scheme 2. A general mechanism for acid-catalyzed dimerization of AMS.

procedure required use of organic solvents to form a homogenous catalysis. Recently, Shan et al. reported a solvent-free procedure for preparation of Indan from AMS. However, an extremely moisture-sensitive Lewis acidic ionic liquid Et₃NHCl-AlCl₃ was used as catalyst.³ Reaction temperature was screened for conversion of chain isomers into Indan with $[Hmim]^+BF_4^-/AMS = 1:2 \pmod{mol}$. The results were compiled in Table 4. From Table 4, it looked like that conversion of both 1-PT and 2-PT into Indan was slow at reaction temperature ranging from 120–150 °C. For example, at 120 and 150 °C, Indan, among the dimers, just increased from 41 and 76% to 54 and 88%, respectively, when the reaction time was prolonged from 8 to 48 h (Table 4, entries 1–4). The similar trend was also observed even at higher temperature 170 °C. For example, no AMS remained in the system within 4 h and distribution of dimers was 89% Indan, 5% 1-PT and 6% 2-PT. Under this condition, both 1-PT and 2-PT were slowly converted into Indan and disappeared after 18 and 30 h, respectively, (Table 4, entries 5-10). It is clear that, at higher reaction temperature, the dimerization produces Indan as the major product and the minor isomers 1-PT and 2-PT could be converted into Indan ultimately. Compared with the recently reported dimerization of AMS catalyzed by Brönsted and Lewis acid ionic liquids, advantages of our procedure are obvious: the ionic liquid [Hmim]⁺BF₄⁻ was readily available and air and moisture stable, and more importantly, both of two useful products could be obtained in high selectivity.

Table 4. Cyclolization of AMS catalyzed by [Hmim]⁺BF₄^{-a}

Entry	<i>T</i> (°C)	Time (h)	Conv. (%)	Distribution of dimers (%) ^b		
				Indan	1-PT	2-PT
1	120	8	100	41	43	16
2	120	48	100	54	25	21
3	150	8	100	76	13	11
4	150	48	100	88	2	10
5	170	4	100	89	5	6
6	170	8	100	91	2	7
7	170	12	100	93	1	6
8	170	18	100	97		3
9	170	24	100	98		2
10	170	30	100	100	_	_

^a Reaction was carried out with [Hmim]⁺BF₄⁻/AMS=1:2 (mol/mol). ^b Determined by GC.

3. Conclusion

In conclusion, we described a Brönsted acidic ionic liquid catalyzed and temperature-controlled highly selective dimerization of α -methylstyrene to produce widely used chemicals in polymers: 2,4-diphenyl-4-methyl-1-pentene and the saturated cyclic isomer, 1,1,3-trimethyl-3-phenyl-indan. At low reaction temperature, such as 60 °C, 2,4-diphenyl-4-methyl-1-pentene was formed in 93% selectivity with >92% conversion using 25 mol% [Hmim]⁺BF₄⁻ under a solvent-free condition while Indan could be obtained in 100% selectivity when the reaction temperature was increased to 170 °C. The ionic liquid [Hmim]⁺BF₄⁻ was recycled six times showing no decrease of activity after the mention of quantity loss of the ionic liquid during work-up procedure.

4. Experimental

All commercial chemicals were used without further purification. Ionic liquid $[Hmim]^+BF_4^-$ was prepared according to the reported procedure.^{6c} GC and GC-Mass analyses were performed on a HP-Agilent 6890 with a 30 m Hp-5MS column. ¹H NMR spectra were acquired on a Bruker Avance 500 spectrometer in CDCl₃ using TMS as internal standard.

4.1. General procedure for the dimerization of α-methylstyrene (AMS)

To a 25 mL flask charged with a magnetic stirrer and a reflux condenser was added 1.7 g (10 mmol) [Hmim]⁺BF₄ and 2.4 g (20 mmol) α -methylstyrene. The resulting biphasic mixture was heated in oil bath at designed temperature under N₂. After being cooled to room temperature, the organic layer was separated from the ionic liquid by decanting. Composition of products was analyzed by GC and compared with authentic samples. Mass balances (>95%) were obtained in all cases and only traces of organics (substrate AMS and products) were found remained in ionic liquid phase, which was removed by wash with hexane in the recycling of the ionic liquid.

4.1.1. 2,4-Diphenyl-4-methyl-1-pentene. ¹H NMR (CDCl₃, 500 MHz) δ : 1.30 (s, 6H, CH₃), 2.91 (s, 2H, CH₂), 4.89 (d, J = 1.8 Hz, 1H, =CH₂), 5.22 (d, J = 1.8 Hz, 1H, =CH₂), 7.19–7.30 (m, 10H, Ph); MS (EI) *m/z*: 236 [M]⁺, 221 [M-CH₃]⁺, 119, 91, 77.

4.1.2. 1,1,3-Trimethyl-3-phenylindan. ¹H NMR (CDCl₃, 500 MHz) δ : 1.03 (s, 3H, CH₃), 1.34 (s, 3H, CH₃), 1.68 (s, 3H, CH₃), 2.19 (d, *J*=13 Hz, 1H, CH_{2a}), 2.42 (d, *J*=13 Hz, 1H, CH_{2b}), 7.10–7.27 (m, 9H, Ph). MS (EI) *m/z*: 236 [M]⁺, 221 [M-CH₃]⁺, 143, 128, 91, 77.

Acknowledgements

Project supported by the National Natural Science Foundation of China (No. 20172016), Shanghai Science and Technology Council (No. 01QA14017, 02QA14016 and 04JC14032).

References and notes

- 1. Chaudhuri, B. Org. Process Res. Dev. 1999, 3, 220-223.
- Gerhard, M.; Yang, D.; Oskar, N. Macromol. Chem. Phys. 1994, 195, 3721–3733.
- 3. Cai, Q.; Li, J.; Bao, F.; Shan, Y. Appl. Catal. 2005, 279, 139–143 and references therein.
- 4. Zhou, Q. Suliao 1992, 21, 28-31 (in Chinese).

- (a) Welton, T. Chem. Rev. 1999, 99, 2071–2083. (b) Welton, T. Coord. Chem. Rev. 2004, 248, 2459–2477. (c) Olivier-Bourbigou, H.; Magna, L. J. Mol. Catal. A: Chem. 2002, 182–183, 419–437.
- (a) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weave, K. J.; Forbes, D. C.; Davis, J. H. J. Am. Chem. Soc. 2002, 124, 5962–5963. (b) Wu, H.-H.; Yang, F.; Cui, P.; Tang, J.; He, M.-Y. Tetrahedron Lett. 2004, 45, 4963–4965. (c) Zhu, H.-P.; Yang, F.; Tang, J.; He, M.-Y. Green Chem. 2003, 5, 38–39.
- 7. Gu, Y. L.; Shi, F.; Deng, Y. Q. Catal. Commun. 2003, 4, 597–601.
- Zang, P. R.; Du, J. Y.; Yang, F.; Zou, G.; Tang, J. Chin. J. Chem. 2005, 23, 581–583.