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Lanthanum Triflate-Catalyzed Rapid Oxidation of Secondary Alcohols Using Hydrogen Peroxide Urea Adduct (UHP) in Ionic Liquid

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LANTHANUM TRIFLATE-CATALYZED RAPID OXIDATION OF SECONDARY ALCOHOLS USING HYDROGEN PEROXIDE UREA ADDUCT (UHP) IN IONIC LIQUID

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GRAPHICAL ABSTRACT



Abstract A convenient and efficient protocol for the oxidation of secondary hydroxyl group to ketone using hydrogen peroxide–urea adduct and catalytic $(CF_3SO_3)_3La$ in ionic liquid has been developed. A number of 1,2-diols, α -hydroxyketones, and other aromatic and aliphatic secondary alcohols have been successfully oxidized to the corresponding ketones using this protocol in good yields and short reaction times.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications[®] for the following free supplemental resource(s): Full experimental and spectral details.]

Keywords Ionic liquid; ketones; lanthanum triflate; oxidation; secondary alcohols; UHP

INTRODUCTION

Oxidation of alcohols to carbonyl compounds is a fundamental reaction in organic chemistry and several methods have been reported in the literature covering a wide variety of reagents.^[1] Recently $Fe(NO_3)_2 \cdot 9H_2O$,^[2] NBS/2,6-lutidine,^[3] 1,4-diazabicyclo[2.2.2]octane (DABCO) / Br_2 ,^[4] N-bromosuccinimide (NBS)-CCl₄-Py,^[5] NBS-Al₂O₃,^[6] and 4-MeO-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)^[7] have been used to accomplish this transformation. However, some of these catalytic systems

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are performed in aromatic or halogenated solvents or have drawbacks in terms of cost of reagents, harsh reaction conditions, poor yields, environmentally unfriendly oxidants, or wastes.^[8] Recently much attention has been directed toward the reduction or replacement of volatile organic compounds (VOCs) from the reaction media because of environmental concerns.^[9] A variety of environmentally benign media, such as water, ionic liquids, and supercritical fluids, have been promoted as replacements to VOCs. Ionic liquids have been recognized as promising green solvents because of their unique properties, including low volatility, high polarity, good stability over a wide temperature range, and capacity to dissolve a variety of organic, inorganic, and organometallic compounds. Furthermore, the proper choice of cations and anions for an ionic liquid can allow for fine-tuning of their miscibility with water and organic solvents to simplify separation processes by liquid-liquid extraction.^[10] The advantages of ionic liquids as reaction media for transition-metal-catalyzed oxidations has yet to be widely explored. Also, the development of new catalytic oxidation system using urea-hydrogen peroxide adduct (UHP) as terminal oxidant is particularly attractive as replacing H2O2 by its urea adduct requires a simple reaction setup.^[11] Thus, we explored the possibility

RESULTS AND DISCUSSION

ketones, and alcohols.

In this article, we report a rapid and environmentally benign protocol for the oxidation of a variety of 1,2-diols, α -hydroxyketones, and other secondary alcohols using hydrogen peroxide–urea adduct (UHP) as the oxidant and lanthanum triflate as the catalyst in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄). The reaction conditions were optimized by attempting reactions of hydrobenzoin (1a) (1.0 mmol) with UHP (2.0 mmol) in different ionic liquids and different catalysts. The reactions attempted in different ionic liquids using InCl₃ (10 mmol%) as catalyst gave poor yields, though among these greatest yield was obtained in [bmim]BF₄ (Table 1, entries 1–4). Subsequently, other catalysts namely, L-proline, DBU

of using urea-H₂O₂ adduct in ionic liquids for the oxidation of 1,2-diols, α -hydroxy

Entry	Ionic liquid	Catalyst	Time (h)	Yield ^b (%) 30	
1.	[bmim]Cl	InCl ₃	6		
2.	[bmim]BF ₄	InCl ₃	6	55	
3	[bmim]PF ₆	InCl ₃	6	40	
4	[bmim]Br	InCl ₃	6	35	
5.	[bmim]BF ₄	L-Proline	6	20	
6.	[bmim]BF ₄	DBU	6	25	
7	[bmim]BF ₄	CTAB	6	20	
8.	[bmim]BF ₄	(CF ₃ SO ₃) ₃ La	1.5	90	

Table 1. Optimization of the reaction conditions for oxidation of hydrobenzoin to benzil^a

"Employing 1.0 mmol hydrobenzion, 10 mol% catalyst, 2.0 mmol UHP, and 5 mmol ionic liquid at 70 °C.

^bIsolated yields.



(1,8-diazabicyclo-[5.4.0]undec-7-ene), cetyltrimethylammonium bromide (CTAB), and lanthanum triflate were screened in [bmim]BF₄ to identify optimal conditons. While reactions in the presence of DBU, CTAB, and L-proline gave poor product yields (Table 1, entries 5–7), the reaction in the presence of lanthanum triflate proved to be the best with 90% yield of benzil (**2a**) using 1:2 molar ratio of substrate–UHP (Table 1, entry 8). It was further observed that though the reaction of hydrobenzoin was complete using 1:1 molar ratio of substrate–UHP, it yielded a mixture of benzoin and benzil. Increasing the molar ratio of hydrobenzoin–UHP to 1:3 had no marked effect on the product yield or time of the reaction. Reactions at higher temperatures affected the oxidation adversely in terms of yield of the benzil, probably due to rapid decomposition of H_2O_2 at higher temperature.

Subsequently, oxidation of different hydrobenzoins was carried out under optimized reaction conditions (Table 2, entries 1–9). All reactions were clean and gave the corresponding substituted benzils in good yields.

Entry	Substrate	UHP (equiv.)	Time (min.)	Product	$\operatorname{Yield}^{b}(\%)$	MP (found)	MP (literature)
1	1a	2	60	2a	90	92–94	92-94 ^[12]
2	1b	2	30	2b	94	104-105	103-104 ^[12]
3	1c	2	40	2c	87	196–198	198-199 ^[12]
4	1d	2	45	2d	89	120-124	128-130 ^[12]
5	1e	2	40	2e	90	90-92	91-93 ^[13]
6	1f	2	35	2f	91	118-120	121-122 ^[12]
7	1g	2	40	2g	90	114-116	116–117 ^[14]
8	1ĥ	2	180	2h	75	32-34	34-38 ^[15]
9	1i	2	150	2i	78	78-80	82-83[16]
10	3a	2	45	2a	93	92–94	92–94 ^[12]
11	3b	2	30	2b	89	103-104	103-104 ^[12]
12	3c	2	40	2c	90	199-200	198–199 ^[12]
13	3d	2	50	2d	87	124-126	128-130 ^[12]
14	3e	2	35	2e	85	90-92	91–93 ^[13]
15	3f	2	30	2f	90	118-120	121-122 ^[12]
16	4 a	3	45	5a	92	48-50	47-49 ^[17]
17	4b	3	30	5b	91	144-146	144–145 ^[18]
18	4c	3	40	5c	80	78-80	79-80 ^[19]
19	4d	2	50	5d	84	Liquid	
20	4 e	2	55	5e	80	50-52	48-52[20]
21	4 f	2	90	5f	82	106-108	109-110 ^[21]
22	4g	2	50	5g	82	Liquid	_
23	4h	2	60	5h	84	Liquid	
24	4 i	2	120	5i	78	Liquid	_
25	4j	2	120	5j	74	Liquid	_
26	4k	3	50	5k	95	80-82	82-83[22]
27	41	2	120	51	80	Liquid	_

Table 2. Oxidation of secondary alcohols using 10 mol% lanthanum triflate as catalyst and UHP as oxidant in bmim[BF₄]^{*a*}

^{*a*}Reaction using 1.0 mmol alcohol, UHP, 10 mol% (CF₃SO₃)₃La, and 5 mmol [bmim]BF₄ at 70 $^{\circ}$ C for the appropriate time.

^bIsolated yield.



OXIDATION OF SECONDARY ALCOHOLS



The application of UHP as an oxidant for the oxidation of α -hydroxyketones in [bmim]BF₄ was also investigated. α -Hydroxyketones also underwent oxidation using 1:2 molar ratio of substrate–UHP in [bmim]BF₄ at 70 °C to give the corresponding 1,2-diketones in good yields (Table 2, entries 10–15). Reaction using 1:1 molar ratio of benzoin to UHP was incomplete even after a prolonged reaction time.

The efficiency of this method was further evaluated for oxidation of alcohols. It was observed that benzhydrols could be oxidized to corresponding benzophenones in good yields (Table 2, entries 16–18). Similarly other aromatic alcohols and aliphatic alcohols could be oxidized to corresponding ketones (Table 2, entries 19–27). The reactions of diaryl alcohols required 3 molar equivalents of UHP for completion of reaction.

$$\begin{array}{c} \mathsf{R}-\mathsf{CH}-\mathsf{R'} & \underbrace{\mathsf{UHP}, \ 10 \ \text{mol}\% \ (\mathsf{CF}_3\mathsf{SO}_3)_3\mathsf{La}}_{[bmim]} \mathsf{BF}_{4,}70^{\circ}\mathsf{C}} & \mathsf{R}-\mathsf{C}-\mathsf{R'} & (3) \\ \hline \mathbf{4} & \mathbf{5} \\ \mathbf{a}) \ \mathsf{R}=\mathsf{R'}=\mathsf{C}_6\mathsf{H}_5 & \mathsf{b}) \ \mathsf{R}=\mathsf{R'}=\ 4\text{-}\mathsf{ClC}_6\mathsf{H}_4 \\ \mathsf{c}) \ \mathsf{R}=\mathsf{C}_6\mathsf{H}_5, \ \mathsf{R'}=4\text{-}\mathsf{BrC}_6\mathsf{H}_4 & \mathsf{d}) \ \mathsf{R}=\mathsf{C}_6\mathsf{H}_5, \ \mathsf{R'}=\mathsf{CH}_3 \\ \mathsf{e}) \ \mathsf{R}=4\text{-}\mathsf{BrC}_6\mathsf{H}_4, \ \mathsf{R'}=\mathsf{CH}_3 & \mathsf{f}) \ \mathsf{R}=4\text{-}\mathsf{ClC}_6\mathsf{H}_4, \ \mathsf{R'}=\mathsf{CH}_3 \\ \mathsf{g}) \ \mathsf{R}=4\text{-}\mathsf{ClC}_6\mathsf{H}_4, \ \mathsf{R'}=\mathsf{CH}_3 & \mathsf{h}) \ \mathsf{R}=4\text{-}\mathsf{CH}_3\mathsf{C}_6\mathsf{H}_4, \ \mathsf{R'}=\mathsf{CH}_3 \\ \mathsf{h}) \ \mathsf{R}=\mathsf{C}_6\mathsf{H}_{13}, \ \mathsf{R'}=\mathsf{CH}_3 & \mathsf{h}) \ \mathsf{R}=\mathsf{C}_2\mathsf{H}_5, \ \mathsf{R'}=\mathsf{C}_{\mathsf{H}_5} \\ \mathsf{k}) \ \mathsf{R}-\mathsf{R'}=9\text{-}\mathsf{Fluorenyl} & \mathsf{l}) \ \mathsf{R}=\mathsf{R'}=-(\mathsf{CH}_2)_{5} \end{array}$$

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EXPERIMENTAL

All the chemicals purchased from Sigma-Aldrich were used as received. All the products are known and were identified by co-TLC with authentic samples and by mp (wherever applicable). Silica gel 60 F_{254} (precoated aluminium plates) from Merck were used to monitor the reaction progress. Melting points were determined on a Tropical Labequip apparatus and are uncorrected. Infrared (IR) (KBr) spectra were recorded on a Perkin-Elmer FTIR spectrophotometer. The ¹H NMR spectra were recorded on a Hitachi FT-NMR model R-600 (60 MHz) using tetramethylsilane (TMS) as an internal standard. The ionic liquids were synthesized by reported procedures.^[23,24] The products were identified by co-TLC with authentic samples, mp, mixed mp (wherever applicable), and spectral data.

Typical Procedure for the Oxidation of 4,4'-Dimethylhydrobenzoin (1b) as a Representative Example

In a typical experiment, a mixture of 4,4'-dimethylhydrobenzoin (1b) (1.0 mmol), UHP (2.0 mmol), 10 mol% (CF₃SO₃)₃La, and [bmim]BF₄ (5 mmol) was placed in a 50-mL, round-bottom flask fitted with a calcium chloride guard tube. The reaction mixture was stirred magnetically in an oil bath maintained at 70 °C for 30 min. (Table 2). The progress of the reaction was monitored by TLC using petroleum ether–ethyl acetate (70:30). After completion of the reaction, the reaction mixture was cooled to room temperature and washed with diethyl ether (3 × 10 mL). The combined ethereal layer was washed with water (2 × 10 mL) and dried over anhydrous. Na₂SO₄. The ethereal extract was concentrated on a rotary evaporator to give a white solid, which was identified as 4,4'-dimethylbenzil by mp, IR, and ¹H NMR spectra.

Yield (94%); mp 104–105 °C (lit. 103–104^[12]); IR (KBr, cm⁻¹): $\nu_{max} = 2919$, 1661, 1605, 1172; ¹H NMR (60 MHz, CDCl₃) δ 7.86 (d, J = 8.0 Hz, 4H, Ar), 7.30 (d, J = 8.0 Hz, 4H, Ar), 2.43 (s, 6H, CH₃).

Supporting Information

General procedures for the oxidation of 1,2-diols, α -hydroxyketones, and other aromatic or aliphatic secondary alcohols are available in the Supporting Information.

CONCLUSION

We have reported a mild, efficient, and green catalytic oxidation procedure for the oxidation of hydrobenzoins, α -hydroxyketones, and alcohols to the corresponding benzils and ketones.

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