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Article

I₂/ionic liquid as a highly efficient catalyst for per-*O*-acetylation of sugar under microwave irradiation

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ABSTRACT

A practical and highly efficient approach was developed to synthesize peracetylated sugar derivatives using a recyclable iodine/PEG₄₀₀-based ionic liquid catalyst (I₂/IL). The peracetylated sugars were readily obtained in a few minutes in excellent yields (90%–99%, 13 examples) on a multi-gram scale (50.0 mmol) by the reaction of sugar and acetic anhydride under microwave irradiation in the absence of a volatile organic solvent. The desired product was easily obtained by simple extraction with toluene from the reaction mixture, and I₂/ILs can be readily recovered and reused at least six times without obvious loss in the yield. When the scale of the per-*O*-acetylation reaction was increased to 50.0 mmol, the desired product was still obtained in 90% yield after five recycles.

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1. Introduction

Per-*O*-acetylation of sugar is a frequently used transformation in carbohydrate chemistry as it provides an efficient and cheap means for protecting the hydroxy groups of sugars [1]. Peracetylated sugars are widely used as important and inexpensive building blocks to synthesize biologically important oligosaccharides and oligosaccharides and many bioactive natural products [2–5]. Therefore the synthesis of peracetylated sugars is an important topic in the preparation of functional glycoconjugates and oligosaccharides [6,7]. Considerable efforts have been made in the development of efficient and mild strategies for the per-*O*-acetylation of sugars [8–10].

In general, a large excess of acetic anhydride is routinely used as acylating agent and solvent in the presence of an acidic or basic catalyst, such as pyridine [11], sodium acetate [12],

H₂SO₄ [13], and HClO₄ [14]. Although the above catalysts have been widely applied to prepare peracetylated sugars, many of these are associated with several obvious shortcomings, such as environmental toxicity, unpleasant odour, equipment corrosion, formation of unwanted side products, and incompatibility with carbohydrate derivatives containing acid-labile functional groups.

A variety of Lewis acid catalysts such as InCl₃ [15], In(OTf)₃ [16], ZnCl₂ [17], Fe₂(SO₄)₃ [18], FeCl₃ [19], Bi(OTf)₃ [20], Sc(OTf)₃ [21], (CH₃)₃SiOTf [22], Cu(OTf)₃ [23], Ce(OTf)₃ [24], and BF₃·Et₂O [25] have been introduced for the acid catalyzed per-*O*-acetylation of sugars. However, these catalysts also suffer from significant drawbacks, such as expensive reagent, long reaction time, harsh reaction conditions, and difficulty in the recovery and reusability of the catalyst. Solid acid catalysts can mitigate these problems as they are inexpensive and allow the

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straightforward removal of the catalysts from the reaction system [26–30].

Recently, molecular I_2 has drawn considerable attention as an efficient, mild, and readily available Lewis acid catalyst for various organic reactions [31]. In 1997, I_2 was used successfully for the synthesis of per-*O*-acetylated sugars in excellent yield with a short reaction time [32]. However, it is difficult to use I_2 because it has good solubility in most organic solvents and easily sublimate at high temperature. In addition, the used I_2 in the reaction mixture was not recovered. It was difficult to use I_2 in large scale synthesis due to environmental and economic concerns. Therefore, there is a need to find a simple and efficient support for reusable I_2 in the per-*O*-acetylation of sugars.

As a non-conventional energy source, microwave (MW) irradiation leads to a large reduction in reaction time and obvious enhancement in conversion, and has emerged as a useful technology in organic chemistry [33–39]. As a part of our continuing interest in improving the practicability and efficiency of MW irradiation technology [40–43], we report here a simple, rapid, and scalable strategy for the synthesis of per-*O*-acetylated sugars catalyzed by I_2 in PEG400-based ionic liquid (I_2/IL_{400}) under MW irradiation (Scheme 1). IL_{400} is an appealing polar solvent. It is ambience friendly because it has a high boiling point and has low toxicity and is biodegradable. Interestingly, the IL_{400} and toluene system gives heterogeneous phases at room temperature, such that the product can be easily recovered from the reaction mixture by simple extraction with toluene while the catalyst I_2 remains in IL_{400} and can be reused in the next cycle. I_2/IL_{400} can be reused at least six times without significant loss of its catalytic activity. No previous example of a rapid and efficient synthesis of fully acetylated sugars catalyzed by recyclable I_2/IL_{400} has been reported.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were obtained from commercial sources and used without further purification. All the per-*O*-acetylation reactions were carried out in a commercial MW

reactor equipped with a stirring bar and were monitored by TLC. The MW bench top reactor (MAS-II) was manufactured by Sineo Microwave Chemistry Technology (Shanghai) Co. IR spectra were obtained using a Fourier transform infrared (FT-IR, 4000–400 cm^{-1}) spectrometer (Nicolet Nexus FTIR spectrometer, USA) using 4 cm^{-1} resolution and 32 scans. Samples were prepared using the KBr disc method. NMR spectra were acquired in $CDCl_3$ on a Bruker DMX-400 spectrometer at 400 MHz for 1H NMR. The chemical shifts were given in δ values from TMS as an internal standard.

2.2. Preparation of IL_{400}

The revised route for the preparation of IL_{400} is outlined in Scheme 2. To a solution of PEG400 (60 mmol) and Et_3N (120 mmol) in toluene (200 mL) was added methylsulfonyl chloride (120 mmol) dropwise in 30 min under N_2 atmosphere. Then the mixture was stirred at room temperature. After 3 h, the mixture was filtered. The filtrate was added to *N*-methylimidazol (120 mmol), and the mixture was stirred at 80 °C for 30 min under MW irradiation (200 W). After the reaction, the ionic liquid layer was separated and washed with petroleum ether (PE, 3×10 mL). Evaporation of residual PE under reduced pressure gave the desired pure product IL_{400} in 90% yield.

2.3. Typical procedure for per-*O*-acetylation of *D*-glucose

To a 10.0 mL round bottom flask, *D*-glucose (2.0 mmol) and acetic anhydride (12.0 mmol, 1.2 equiv. per OH) in the IL_{400} (2.0 mL) was added I_2 (0.05 mmol) at room temperature. Then the mixture was heated to 50 °C under MW irradiation (200 W) until the TLC analysis showed that the reaction was complete. Then the reaction mixture was cooled to room temperature, and toluene (2.0 mL × 3) was added. The mixture was vigorously stirred for several minutes and then kept stationary. The upper toluene layer containing the product was collected. Toluene was removed by a rotary evaporator, and the crude product was purified by recrystallization in ethyl alcohol. The desired peracetylated sugars were obtained in 90%–99% yields. The bottom phase was the ionic liquid containing the I_2 catalyst

Scheme 1. Synthesis of peracetylated sugars catalyzed by I_2/IL_{400} under MW irradiation.

Scheme 2. Synthesis of IL_{400} by a revised method under MW irradiation.

and produced acetic acid. The I_2/IL_{400} system was reused after the removal of the acetic acid under reduced pressure.

2.4. Typical procedure of the scale up of per-*O*-acetylation of sugars

To a 100 mL round bottom flask, the D-glucose (50 mmol) and acetic anhydride (0.25 mol) in the IL_{400} (20 mL) were added I_2 (0.25 mmol) at room temperature. Then the mixture was heated to 50 °C under MW irradiation (200 W) until the TLC analysis showed that the reaction was complete. The work-up of the reaction mixture was carried out by the same procedure as the model reaction.

3. Results and discussion

3.1. Preparation and characterization of IL_{400}

In general, IL_{400} is prepared by nucleophilic substitution between $CH_3SO_2-OPEG_{400}O-SO_2CH_3$ and substituted imidazoles under conventional heating conditions. However, this synthesis method has an obvious disadvantage in that it needed a long reaction time (several hours to 2 d) and harsh reaction condition (> 80 °C).

In this work, a modified method was developed to synthesize PEG_{400} imidazolium salt ionic liquid, as depicted in Scheme 2. First, $CH_3SO_2-OPEG_{400}O-SO_2CH_3$ was synthesized by a reaction of $HO-PEG_{400}-OH$ with methanesulfonyl chloride using Et_3N as a base in toluene at 0 °C under N_2 atmosphere. After completion of the reaction, the white solid byproduct was removed by filtration. Without any purification, the filtrate was added to 1-methylimidazol, the mixture was then heated to 80 °C under MW irradiation (200 W) for 30 min, and the desired IL_{400} was obtained. Compared to the traditional heating method, the use of MW irradiation dramatically reduced the reaction time. In the synthesis of IL_{400} , the key step was the nucleophilic substitution between $CH_3SO_2-OPEG_{400}O-SO_2CH_3$ and 1-methylimidazol under MW irradiation.

The IL_{400} was characterized using FT-IR and 1H NMR. Figure

1 shows the FT-IR spectra of PEG_{400} and IL_{400} . The peaks at 1043 and 1109 cm^{-1} of IL_{400} were the characteristic absorption bands of S=O. In the case of IL_{400} , the broad band at 2900 cm^{-1} can be attributed to the C–H stretching of the $-CH_2-$ group, and the peak at 1196 cm^{-1} was from the C–O stretch in PEG_{400} . The peak at 3107 cm^{-1} was assigned to C–H stretching of the imidazole ring. The IL_{400} also exhibited other characteristic absorption bands at 1350 cm^{-1} , which was assigned to the symmetric stretching of $-CH_3$. The peaks at 1537 and 1653 cm^{-1} which appeared, were related to the band of C=C and C=N, respectively.

The 1H NMR spectrum (not shown) showed the peaks at 9.48, 7.67, and 7.52 ppm assigned to H_{imid} . The single peak at 3.99 ppm was assigned to the protons of NCH_3 . The peaks between 3.88 and 3.55 ppm were due to $PEG-H$. The single peak at 2.71 ppm was assigned to the protons of $-SO_2CH_3$. The results confirmed the successful preparation of IL_{400} .

3.2. Per-*O*-acetylation of glucose catalyzed by various catalysts

First, the per-*O*-acetylation reaction of glucose with acetic anhydride was chosen as a model reaction to screen the catalysts. The reaction was performed under MW irradiation. The per-*O*-acetylation reaction was simply performed by stirring the mixture of glucose with a slight excess of acetic anhydride (1.2 equiv. per OH), and by using different catalysts in IL_{400} at 50 °C. The results are summarized in Table 1.

The optimization study revealed that per-*O*-acetylated glucose was only obtained in 60% yield using acetic anhydride in the absence of a metal salt catalyst at 50 °C after 3 min under MW irradiation. It was also observed that when the per-*O*-acetylation of glucose was carried out using metal salts catalysts such as $Co(OAc)_2$, $FeCl_3$, $Cu(OAc)_2$, and $ZnCl_2$ under the same condition, per-*O*-acetylated glucose was prepared in moderate yields (67%–77%). To our delight, after the screening experiment with the target catalyst, that is I_2 , the reaction occurred the most efficiently and yielded the product in 99% isolated yield. Thus I_2 was reasonably chosen as the best catalyst for sugar per-*O*-acetylation under MW irradiation due to its high efficiency, low toxicity, and easy recyclability.

Fig. 1. FT-IR spectra of PEG_{400} and IL_{400} .

Table 1

Effect of the various catalysts on the per-*O*-acetylation of glucose with acetic anhydride under MW irradiation.

Entry	Catalyst	Isolated yield (%)
1	—	60
2	$Co(OAc)_2$	73
3	$FeCl_3$	70
4	$Cu(OAc)_2$	77
5	$ZnCl_2$	67
6	I_2	99

Reaction conditions: D-glucose (2.0 mmol), acetic anhydride (1.2 equiv. per OH), and catalyst (5 mol%) in IL_{400} (2.0 mL) at 50 °C for 3 min under MW irradiation (200 W).

3.3. Effect of I_2 concentration on the per-*O*-acetylation of *D*-glucose

To optimize the reaction conditions, we first determined the optimum dosage of catalyst. The acetylation of *D*-glucose was chosen as a model reaction to react with a slight excess of acetic anhydride in the presence of 1.0, 3.0, 5.0, and 7.0 mol% of I_2 in IL₄₀₀ at 50 °C under MW irradiation. The results are summarized in Table 2. To our delight, thin layer chromatography (TLC) showed that the reaction was completed within 3 min in

quantitative conversion rate. A 99% isolated yield was obtained when the catalyst amount was 5.0 mol%; it took a longer time (10 min, 62%) when the catalyst was used in the amount of 1.0 mol%. Thus, the per-*O*-acetylation of sugar was performed in the presence of 5 mol% of I_2 . However, the reaction gave only 60% and 70% yields under I_2 -free conditions and a conventional heating condition, respectively (entries 8 and 9). The results showed that combining the I_2 /IL₄₀₀ catalytic system with the use of microwave irradiation dramatically improved the yield of the reaction.

Table 3

Per-*O*-acetylation of sugars and sugar alcohols using I_2 /IL₄₀₀ as catalyst at 50 °C under MW irradiation.

Entry	Substance	Product	Time ^a (min)	Isolated yield (%)	α/β
1	1a	1b	3	99	1/1.8
2	2a	2b	5	96	2/1
3	3a	3b	4	90	1.3/1
4	4a	4b	5	90	6/1
5	5a	5b	6	96	—
6	6a	6b	10	96	—
7	7a	7b	10	97	4/1
8	8a	8b	12	94	1/1
9	9a	9b	10	93	—
10	10a	10b	10	95	2/1
11	11a	11b	5	93	—
12	12a	12b	5	95	—
13	13a	13b	5	93	—

Reaction conditions: carbohydrate (2.0 mmol), acetic anhydride (1.2 equiv. per OH) and I_2 (5 mol%) in IL₄₀₀ (2.0 mL) at 50 °C under MW irradiation (200 W). ^a Overall time including heating time and incubating time.

Table 2

Optimization of the reaction conditions for the per-*O*-acetylation of D-glucose.

Entry	I ₂ (mol%)	Temperature (°C)	Isolated yield (%)
1	1	50	62
2	3	50	75
3	5	50	99
4	7	50	99
5	5	RT	63
6	5	40	80
7	5	60	99
8	0	50	60
9	5	50	70 ^a

Reaction conditions: glucose (2.0 mmol), acetic anhydride (1.2 equiv. per OH) and I₂ in IL₄₀₀ (2.0 mL) at 50 °C for 3 min under MW irradiation (200 W).

^a Using the traditional heating method.

It is worth mentioning that the reaction mixture was extracted three times with toluene (2.0 mL × 3) and then the obtained toluene solution was titrated with a standard Na₂S₂O₃ solution. It was found that only about 1.5 mg I₂ existed in the toluene, which was obviously lower than in the I₂/IL₄₀₀ catalytic system (25.4 mg). Thus, this makes the process stable, of low toxicity, and cost effective.

From a practical perspective, the I₂/IL₄₀₀ catalytic system should be used in a wide variety of sugars and sugar alcohols. Thus, with the optimum per-*O*-acetylation conditions, the substrate scope of the per-*O*-acetylation reactions between acetic anhydride and various carbohydrate substrates was explored with the I₂/IL₄₀₀ catalytic system (Table 2). The results are summarized in Table 3. The monosaccharides (**1a–4a**), disaccharides (**6a–10a**), and sugar alcohols (**11a–13a**) were peracetylated in excellent yields (90%–99%). Interestingly, saccharide with an acid sensitive protecting group (such as a Schiff base) (**5a**) can also be peracetylated with high yields (96%). In addition, in the case of reducing sugars, the per-*O*-acetylation reactions gave a mixture of α - and β -acetate anomers. In all cases, pure products were obtained by a simple extraction with toluene and recrystallization. The configurations and ratios of these in Table 3 were determined by ¹H NMR spectral analysis (400 MHz). The production of all known compounds gave ¹H NMR spectra that matched data reported in the cited references.

3.4. Reusability of I₂/IL₄₀₀ for per-*O*-acetylation of D-glucose

The recovery and reusability of the catalyst is a very significant factor for a catalytic process. In order to make the I₂/IL₄₀₀ catalytic system highly efficient and economical, we focused on the reusability of I₂/IL₄₀₀ using the per-*O*-acetylation of D-glucose and acetic anhydride. Thus, a set of experiments were performed for the per-*O*-acetylation of D-glucose using a recycled I₂/IL₄₀₀ system. We found that the I₂/IL₄₀₀ system can be easily recovered by extracting the product with toluene and

Fig. 2. Reusability of I₂ in IL₄₀₀ for per-*O*-acetylation of D-glucose.

removing the byproduct acetic acid. After completion of the model reaction in the first run, the product was extracted using toluene, and the I₂/IL₄₀₀ system was easily recovered by removing the acetic acid under reduced pressure without any further purification. Then the I₂/IL₄₀₀ system was subjected to the next reaction cycle with new reactants. As shown in Figure 2, the catalyst can be recycled and reused at least six times without significant loss in product yield (90%–99%).

3.5. Scale up of per-*O*-acetylation of D-glucose catalyzed by I₂/IL₄₀₀

Peracetylated sugars are important building blocks in carbohydrate chemistry, so it is significant for the per-*O*-acetylation to be performed on the many-gram scale. From the excellent results of the I₂/IL₄₀₀ catalytic system, we set out to further investigate the practicality of the system. To extend this strategy to the many-gram scale synthesis, the scale up synthesis of glucopyranose pentaacetate as a model reaction was investigated. As demonstrated in Table 4, we have shown that glucose was peracetylated on 1, 2, and 20 g scales to afford excellent yields. Most importantly, when the scale of the per-*O*-acetylation of glucose was increased to 50.0 mmol, the per-*O*-acetylation was found to proceed successfully and glucopyranose pentaacetate was still obtained in 90% yield even after 6 recycles.

Table 4

Per-*O*-acetylation of D-glucose on large scales.

Entry	Scale (mmol)	Time (min)	Isolated product (g)	Isolated yield (%)
1	2	3	0.8	99
2	5	5	2.0	98
3	50	15	18.5	95
4 ^a	50	15	18.2	93
5 ^b	50	15	18.1	93
6 ^c	50	15	18.0	92
7 ^d	50	15	17.6	90

^a Catalyst was recycled from entry 3 and used for second run.

^b Third run. ^c Fourth run. ^d Fifth run.

3.6. Mechanism of I_2/IL_{400} catalysis of sugars and acetic anhydride

In the acetylation, I_2 served as an extremely powerful catalyst for the per-*O*-acetylation of sugars. The initial step was the activation of acetic anhydride by I_2 to afford a more active intermediate, which reacted faster with the hydroxyl groups on the sugars. In addition, I_2 is also known to absorb microwave energy. Thus, the per-*O*-acetylation reaction can be completed quickly under I_2/IL_{400} and microwave irradiation conditions.

4. Conclusions

We have developed a simple, highly efficient, and eco-friendly method for the per-*O*-acetylation of sugars and sugar alcohols using an I_2/IL_{400} catalytic system under MW irradiation. The I_2/IL_{400} catalytic system was an environmentally benign and reusable catalyst for the per-*O*-acetylation of sugars. This method gave excellent yields, and the I_2/IL_{400} catalytic system can be reused and recovered at least six times with no loss of catalytic performance. When the scale of the per-*O*-acetylation was increased to 50.0 mmol, the peracetylated sugar was still obtained in 90% yield after six recycles. This is remarkable and makes the method economically valuable.

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Graphical Abstract

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I_2 /ionic liquid as a highly efficient catalyst for per-*O*-acetylation of sugar under microwave irradiation

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A mild, practical, and highly efficient approach was developed to synthesize peracetylated sugar derivatives using a recyclable iodine/PEG₄₀₀-based ionic liquid catalyst (I_2/IL_{400}) under microwave irradiation.

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I₂/离子液体作为可回收均相催化剂在微波条件下高效制备全乙酰糖

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摘要: 以可回收的I₂/PEG₄₀₀型离子液体(I₂/IL₄₀₀)为催化体系, 发展了一种高效、实用的合成全乙酰糖衍生物的方法. 结果表明, 以糖与乙酸酐为原料, 在微波辐射、无溶剂条件以及I₂/IL₄₀₀体系中, 数分钟之内可以非常高的产率(90%–99%)和数十毫摩尔规模(50.0 mmol)制备出全乙酰糖. 通过简单的甲苯萃取, 可以从I₂/IL₄₀₀体系中分离出全乙酰糖, I₂/IL₄₀₀体系可循环使用6次, 且产率均在90%以上. 当反应规模扩大到50.0 mmol时, 该体系依然能高效快速地催化糖的全乙酰化, 并且可以循环使用5次, 产率依然维持在90%左右.

关键词: 全乙酰糖; 碘; 离子液体; 微波辐射

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