

## Catalyzed *N*-acylation of carbamates and oxazolidinones by Heteropolyacids (HPAs)

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### Abstract

We wish to report reaction of various carbamates and oxazolidinones with carboxylic acid anhydrides in the presence of Wells-Dawson heteropolyacid catalysis. The *N*-acylation was carried out in presence heteropolyacid catalyst and gave the corresponding *N*-acyl products in good yields under solvent-free, green conditions. In this acylation used of Carboxylic acids and anhydride as acylating agents.

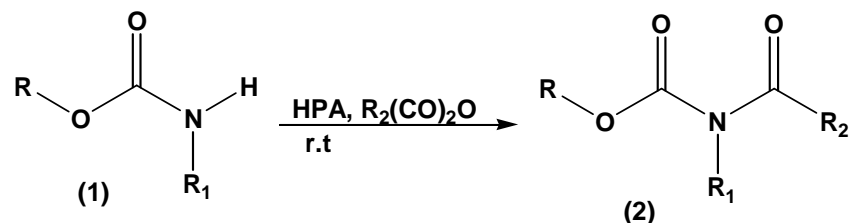
**Keywords:** Wells-Dawson, Heteropolyacid, Acylation, carbamates, oxazolidinones.

For the Friedel–Crafts chemistry, present industrial practice uses acyl chlorides or acid anhydrides as acylating agents and requires a stoichiometric amount of soluble Lewis acids (e.g. AlCl<sub>3</sub>) or strong mineral acids (e.g. HF or H<sub>2</sub>SO<sub>4</sub>) as catalysts, which results in substantial amount of waste and corrosion problems [1]. The overuse of catalyst is caused by-product inhibition—the formation of strong complexes between the aromatic ketone and the catalyst. In view of the increasingly strict environmental legislation, the application of heterogeneous catalysis has become attractive. In the last couple of decades, considerable effort has been put into developing heterogeneously catalysed Friedel–Crafts chemistry using solid-acid catalysts such as zeolites, clays, Nafion-H, heteropolyacids (HPA), etc [1], zeolites being the most studied catalysts [1]. Heteropoly acids are promising solid-acid catalysts for the Friedel–Crafts reactions [2]. They are stronger than many conventional solid acids such as mixed-oxides, zeolites, etc. The Keggin-type HPAs typically represented by the formula H<sub>8-x</sub>[XM<sub>12</sub>O<sub>40</sub>], where X is the heteroatom (most frequently P<sup>5+</sup> or Si<sup>4+</sup>), *x* is its oxidation state, and M is the addenda atom (usually W<sup>6+</sup> or Mo<sup>6+</sup>), are the most important for catalysis [2]. They have been widely used as acid and oxidation catalysts for organic synthesis and found several industrial applications (for a recent comprehensive review, see the monograph [3]). Solid heteropoly acids possess purely Brønsted acidity and are stronger than such conventional solid acids as SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub>, and HX and HY zeolites [2]. The acids H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>], H<sub>4</sub>[SiW<sub>12</sub>O<sub>40</sub>], H<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>], and H<sub>4</sub>[SiMo<sub>12</sub>O<sub>40</sub>] are readily available and most frequently used as acid catalysts, the first two usually being preferred. These acids have fairly high thermal stabilities, decomposing at 465, 445, 375, and 350°C, respectively [4]. *N*-acyl oxazolidinones have found extensive applications in the asymmetric synthesis as chiral auxiliaries [5]. The established methods to obtain these *N*-acyl compounds generally requires NH activation of amide and/or acyl donor, due to the less basic nature of nitrogen atom in carbamates and oxazolidinones compared to the amines. The methods include the reaction of carbamates and oxazolidinones with acid chlorides or anhydrides in basic reaction conditions using the bases such as trialkyl amines, pyridines etc [6]. *N*-Acyl carbamates and oxazolidinones are important synthetic building blocks towards synthesis of bio-active molecules [5,6]. The *N*-acylation of these less nucleophilic compounds has not received

considerable attention under the acidic medium. To our knowledge, only few reports in the literature is described [7]. However, strong acidic conditions *viz.* conc. H<sub>2</sub>SO<sub>4</sub> or HBr/AcOH as well as elevated temperatures are required to achieve such conversions. Recently, *N*-acylation of amides/oxazolidinones with acid anhydrides was demonstrated by the dual activation using MgBr<sub>2</sub>.OEt<sub>2</sub>[8].

## Results and Discussion

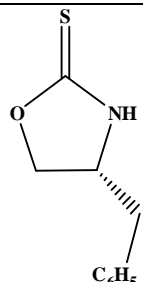
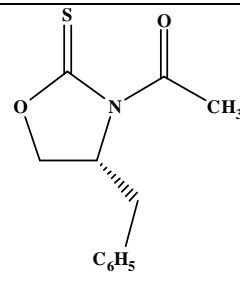
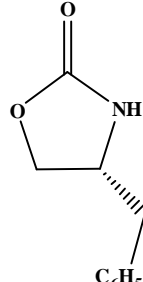
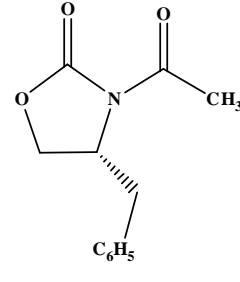
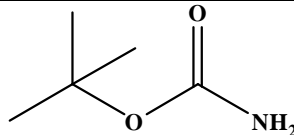
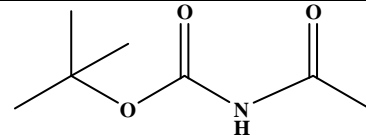
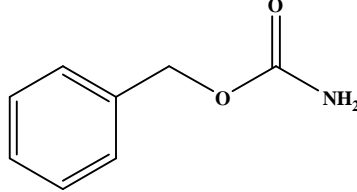
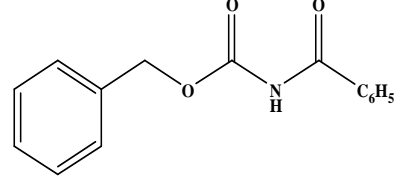
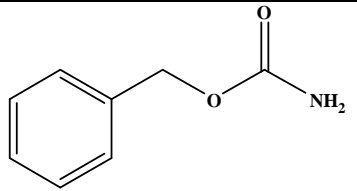
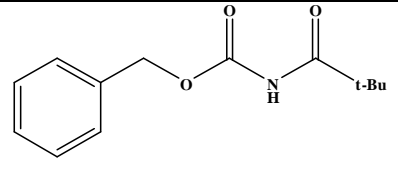
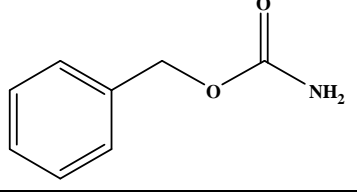
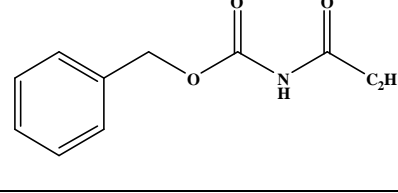
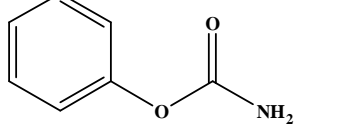
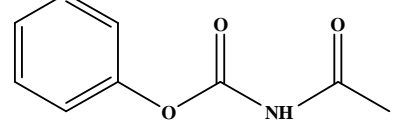
We studied a convenient synthesis of *N*-acyl carbamates and oxazolidinones in the presence of Wells-Dawson heteropolyacid catalyst (Scheme 1).



**Scheme 1.** Synthesis of *N*-acyl carbamates in the presence of Wells-Dawson heteropolyacid catalyst

We continued our researches in acylation and benzyl carbamate **9a**, with acetic anhydride in presence of Wells-Dawson heteropolyacid catalyst under solvent-free and at room temperature conditions afforded the *N*-acetyl benzyl carbamate **9a** in 96% yield (Table 1). In this reaction of acylation, used other acid anhydrides, propionic, pivalic and benzoic anhydrides under similar reaction conditions (Table 1, entries 6a-8a). Phenyl carbamate **8a**, carried out the corresponding *N*-acetyl product in 96% yield (Table 1, entry 8a). oxazolidinone and 1,3-oxazolidine-2-thione were carried out with different anhydrides in the presence of Wells-Dawson heteropolyacid catalyst to obtain the corresponding *N*-acylated products **3a** and **2a** in good yields (Table 1). Acylation of compounds **2a** to **3a** were carried out without any racemization (Table 1, entries 2a, 3a). -Various catalysts were used for *N*-acetylation of benzyl carbamate (**9a**) with acetic anhydride and compared different catalysts with Wells-Dawson heteropolyacid catalyst under room temperature and solvent free condition at different times (Table 1). And the result this synthesis was better and with high yield using of Wells-Dawson heteropolyacid catalyst (Table 1, entry 9a).

**Table 1.** The results of Catalytic activity of the Wells-Dawson heteropolyacid for the *N*-acylation of carbamates and oxazolidinones, in different times

Entry	Carbamate	anhydride	product	Time (min)	<sup>a</sup> Yield (%)
2a		(C <sub>2</sub> H <sub>5</sub> CO) <sub>2</sub> O		45	85
3a		(CH <sub>3</sub> CO) <sub>2</sub> O		25	87
4a		(CH <sub>3</sub> CO) <sub>2</sub> O		10	94
5a		(PhCO) <sub>2</sub> O		120	93
6a		( <i>t</i> -BuCO) <sub>2</sub> O		75	94.5
7a		(C <sub>2</sub> H <sub>5</sub> CO) <sub>2</sub> O		5	97
8a		(CH <sub>3</sub> CO) <sub>2</sub> O		5	98

9a		(CH <sub>3</sub> CO) <sub>2</sub> O		5	96
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<sup>a</sup>Isolated yields. <sup>a</sup>All the products were characterized by <sup>1</sup>H NMR and IR spectra.

**Table 2.** The results of Catalytic activity of various catalysts for the *N*-acetylation of benzyl carbamate (8a) with acetic anhydride, in different times

Entry	Catalyst	Time (min)	<sup>a</sup> Yield (%)
1	H <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ]	10	93
2	H <sub>4</sub> [SiW <sub>12</sub> O <sub>40</sub> ]	15	91
3	H <sub>3</sub> [PMo <sub>12</sub> O <sub>40</sub> ]	25	87.5
4	H <sub>4</sub> [SiMo <sub>12</sub> O <sub>40</sub> ]	25	84
5	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	15	84.5
6	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	10	86
7	H <sub>2</sub> SO <sub>4</sub>	25	70
8	HY-Zeolit	25	71.5
9	H <sub>3</sub> PO <sub>4</sub>	30	63

<sup>a</sup> isolated yields.

**Table 3.** Selected spectra data for compounds 6a-8a

Entry	Compound	IR Vmaxcm <sup>-1</sup> (KBr disk)	<sup>1</sup> H NMR δ (ppm) Solvent (CDCl <sub>3</sub> )
1	Benzyl pivaloylcarbamate (6a)	3296, 2964, 1772, 1687, 1515, 1209, 1165, 700	7.70 (br s, 1H), 7.44-7.32 (m, 5H), 5.20 (s, 2H), 1.23 (s, 9H)
2	Benzyl propionylcarbamate(7a)	3261, 3187, 1756, 1696, 1526, 1195, 1048	7.60 (br s, 1H), 7.39-7.34 (m, 5H), 5.18 (s, 2H), 2.79 (q, <i>J</i> = 7.4 Hz, 2H), 1.16 (t, <i>J</i> = 7.4 Hz, 3H)
3	Phenyl acetylcarbamate (8a)	3257, 3197, 1769, 1704, 1531, 1483, 1220, 1117, 729	8.10 (br s, 1H), 7.46-7.35 (m, 2H), 7.33-7.22 (m, 1H), 7.20-7.12 (m, 2H), 2.49 (s, 3H)

IR, <sup>1</sup>HNMR spectral data of these known compounds were identical with the reported data.

## Conclusion

In summary, the Wells–Dawson H<sub>6</sub>[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>], as an example of Keggin-type heteropolyacid, is an inexpensive, reusable and green catalyst for this reaction. In addition, as a non-hygroscopic, non-corrosive and a water stable solid acid, the handling of this catalyst is easy. It makes this catalyst suitable for the large-scale operation. The reaction appears to be heterogeneously catalyzed. High yields, relatively short reaction times, simplicity of operation and easy work-up procedure are some other advantages of this protocol. This reaction was mild, clean, green, ecofriendly and environmentally friendly.

## References

- [1] P. Metivier, in: R. A. Sheldon, H. van Bekkum (Eds.), *Fine Chemicals Through Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2001, p. 161.
- [2] Y. Izumi, K. Urabe, M. Onaka, *Zeolite, Clay and Heteropoly Acid in Organic Reactions*, Kodansha/VCH, Tokyo, 1992.
- [3] I. V. Kozhevnikov, *Catalysts for fine chemicals*, in: *Catalysis by Polyoxometalates*, vol. 2, Wiley, Chichester, 2002.
- [4] I. V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [5] T. S. Gardner, E. Wenis, J. Lee, *J. Org. Chem.* 19(1954) 753.
- [6] a) W. J. Brouillette, E. E. Smisson, G. L. Grunewald, *J. Org. Chem.* 44(1979) 839.
- [7] D. A. Evans, M. D. Ennis, D. J. Mathre, *J. Am. Chem. Soc.* 104(1982) 1737.
- [8] S. Yamada, S. Yaguchi, K. Matsuda, *Tetrahedron Lett.* 43(2002) 647.

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