



# Catalyst-free esterification of alcohols using 2-acyl-4,5-dichloropyridazinones under microwave conditions



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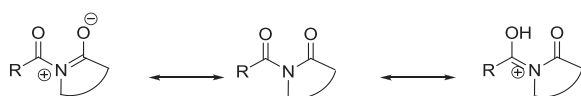
## ABSTRACT

Efficient and green esterification is of great importance. In this work, we demonstrate the catalyst-free esterification of alcohols by their reaction with 2-acyl-4,5-dichloropyridazin-3(2H)-ones under microwave irradiation. Aliphatic and aromatic alcohols were converted into the corresponding esters in good to excellent yields under microwave irradiation in solvent or solvent-free conditions. It is noteworthy that the reaction is catalyst-free, atom-economic, and rapid and that the process is inexpensive.

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## 1. Introduction

*N*-Acylozinones such as 2-acylpyridazinones<sup>1–4</sup> are useful acyl sources in synthesis, and they contain two carbonyl functional groups in the form of a 1,3-diketone system. The reactivities of their two carbonyl groups are different due to the delocalization of the nitrogen lone pair electrons in the azinone ring. One carbonyl group is therefore more reactive for the reaction of nucleophiles. Among the three structures in Scheme 1, the resonance structure on the left includes the most reactive carbonyl group.

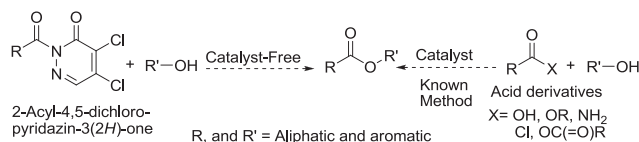


R = Aliphatic and aromatic

Scheme 1. Resonance structures of *N*-acylozinone.

The difference in reactivity between the two carbonyl groups may be usefully exploited in the acylation of alcohols. While the esterification of carboxylic acid derivatives requires a catalyst and/or additives,<sup>5</sup> the esterification of *N*-acylozinones with alcohol may be carried out under catalyst-free conditions to give the corresponding ester and recyclable azinone as the leaving moiety (Scheme 2).

Inspired by recent reports of the acylation of various nucleophiles,<sup>6–11</sup> we selected 2-acyl-4,5-dichloropyridazin-3(2H)-ones as model compounds to evaluate the above hypothesis. 2-Acyl-4,5-dichloropyridazin-3(2H)-ones are inexpensive and good acylating agents, and they can be easily prepared from 4,5-dichloropyridazin-3(2H)-one.<sup>1–4</sup>



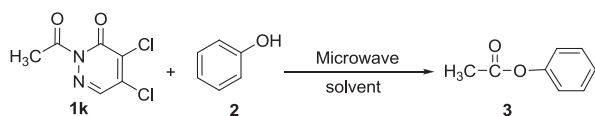
Scheme 2. Conversion of 2-acyl-4,5-dichloropyridazin-3(2H)-ones and acid derivatives into esters.

Since pyridazin-3(2H)-one readily forms stable anion,<sup>6–11</sup> it also acts as a good leaving group. In addition reactions, pyridazin-3(2H)-ones can be removed and/or recycled during synthesis. Herein, we report the catalyst-free conversion of 2-acyl-4,5-dichloropyridazin-3(2H)-ones into esters under microwave (MW) irradiation conditions.

## 2. Results and discussion

Initially, we optimized a model reaction between 2-acetyl-4,5-dichloropyridazin-3(2H)-one (**1k**) and phenol under MW irradiation (Table 1). Based on the findings, we selected THF or solvent-free conditions with microwave irradiation at 150 °C in order to evaluate the reactivity of acetic acid derivatives.

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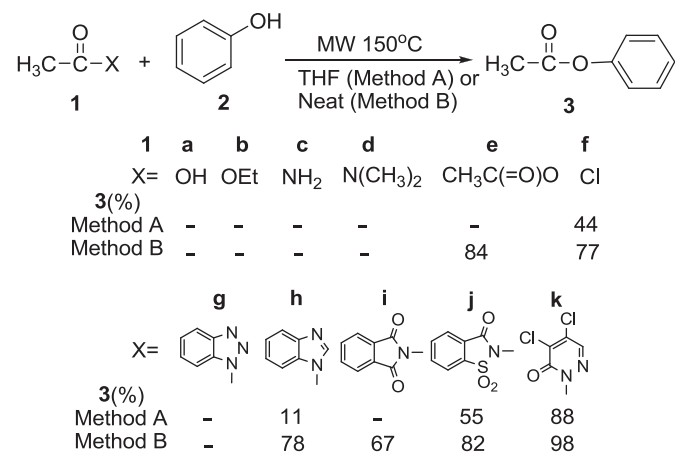
**Table 1**  
Optimization for the conversion of **1k** into ester **3<sup>a</sup>**

Entry	Solvent	Temp (°C)	Time (min)	Ester <b>3<sup>b</sup></b> (%)
1	<i>n</i> -Hexane	150	60	67
2	1,4-Dioxane	150	60	—
3	Benzene	150	40	78
4	Toluene	150	40	83
5	Diethyl ether	150	40	87
6	Acetone	150	40	77
7	DMF	150	40	43
8	Water	150	40	—
9	THF	170	40	71
10	THF	150	40	88
11	THF	130	40	31
12	THF	100	40	14
13	THF	50	40	7
14	THF	25	40	7
15	THF	150	30	—
16	THF	150	20	—
17	THF	150	10	—
18	THF	150	5	88
19	THF	150	10	88
20	—	150	5	98
21	—	170	10	71

<sup>a</sup> Reaction conditions: **2** (1 equiv) and **1k** (1 equiv) in 5 mL of solvent (except for entries 20 and 21) under MW irradiation (300 W).

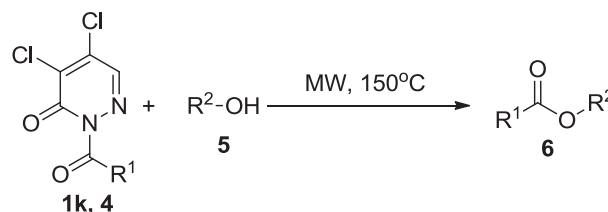
<sup>b</sup> Isolated yields.

Next, we evaluated the reactivity of acetic acid and 10 derivatives: acetic acid (**1a**), ethyl acetate (**1b**), acetamide (**1c**), *N,N*-dimethylacetamide (**1d**), acetic anhydride (**1e**), acetyl chloride (**1f**), 1-acetylbenzotriazole (**1g**), 1-acetyl-1*H*-benzo[*d*]imidazole (**1h**), *N*-acetylphthalimide (**1i**), 1-acetylsaccharin (**1j**), and 2-acetyl-4,5-dichloropyridazin-3(2*H*)-one (**1k**), under the aforementioned conditions. Among the 11 compounds, **1k** showed the best results without THF under MW irradiation (Scheme 3). This result validates our hypothesis. Although **1i** and **1j** are both *N*-acylazinones with the  $-C(=O)NC(=O)-$  unit, **1k** may react more favorable than **1i** and **1j** in this reaction owing to the stability of pyridazin-3-olate.

**Scheme 3.** Reaction of acetic acid derivatives **1** with phenol (**2**) in THF or without THF at 150 °C under MW irradiation.

Based on the preliminary experiments, we selected the following for the optimized system: **1k** (1.2 equiv), ROH (1 equiv), MW (300 W), 150 °C, run time of 5 min, hold time of 5 min, and with or without a solvent. To illustrate the versatility of the catalyst-free esterification, we converted 2-alkanoyl(or aroyl)-4,5-dichloropyridazin-3(2*H*)-ones **1k** and **4**, using aliphatic or aromatic alcohols **5** under

catalyst-free conditions, into the corresponding esters **6** in good to excellent yields (except for 3-hydroxypyridine and benzeneselenol; entries 6 and 7, respectively, in Table 2). In the reactions of 2-acetyl-4,5-dichloropyridazin-3(2*H*)-one with 3-hydroxypyridine and benzeneselenol, the yields in THF were higher than those under

**Table 2**  
Conversion of several 2-acyl-4,5-dichloropyridazin-3(2*H*)-ones into the corresponding esters **6<sup>a</sup>**

Entry	R <sup>1</sup>	R <sup>2</sup>	Ester <b>6<sup>b</sup></b> (%)
1	CH <sub>3</sub>		<b>6a</b> (86) <sup>c</sup>
2	CH <sub>3</sub>		<b>6b</b> (80)
3	CH <sub>3</sub>		<b>6c</b> (93)
4	CH <sub>3</sub>		<b>6d</b> (96)
5	CH <sub>3</sub>		<b>6e</b> (90)
6	CH <sub>3</sub>		<b>6f</b> (45(97)) <sup>d</sup>
7	CH <sub>3</sub>		<b>6g</b> (48(60)) <sup>e</sup>
8			<b>6h</b> (98)
9			<b>6i</b> (72)
10			<b>6j</b> (88)
11			<b>6k</b> (98)
12	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub>		<b>6l</b> (99)
13		CH <sub>3</sub> CH <sub>2</sub> -	<b>6m</b> (92)
14		(CH <sub>3</sub> ) <sub>2</sub> CH-	<b>6n</b> (94)

<sup>a</sup> Reaction conditions: **1k** or **4** (1.2 equiv), ROH (1 equiv), MW (300 W), 150 °C, run time of 5 min, hold time of 5 min, and solvent-free (or in solvent for entries 6 and 7).

<sup>b</sup> Isolated yields. 4,5-Dichloropyridazin-3(2*H*)-one was converted quantitatively.

<sup>c</sup> We used 2 equiv of **1k**.

<sup>d</sup> Reaction of **1k** with 3-hydroxypyridine in THF produced a 97% yield of ester.

<sup>e</sup> Reaction of **1k** with benzeneselenol in THF produced a 60% yield of ester.

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