Tetrahedron Letters 57 (2016) 1843–1846

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of 1-naphthaldehydes via the cascade reactions of 1-phenylpent-4-yn-2-ols promoted by iodine monochloride

Bin Li, Nana Shen, Xuesen Fan *, Xinying Zhang

School of Environment, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, China

ARTICLE INFO

Article history:
Received 5 January 2016
Revised 12 March 2016
Accepted 15 March 2016
Available online 15 March 2016

Keywords:
1-Naphthaldehydes
Iodine monochloride
Cascade reaction

ABSTRACT

A novel and convenient synthesis of 1-naphthaldehydes through iodine monochloride promoted cascade reactions of 1-phenylpent-4-yn-2-ols is presented. Compared with literature procedures, this new method has advantages such as simple operation procedure, mild reaction conditions, good efficiency, and excellent regio-selectivity.

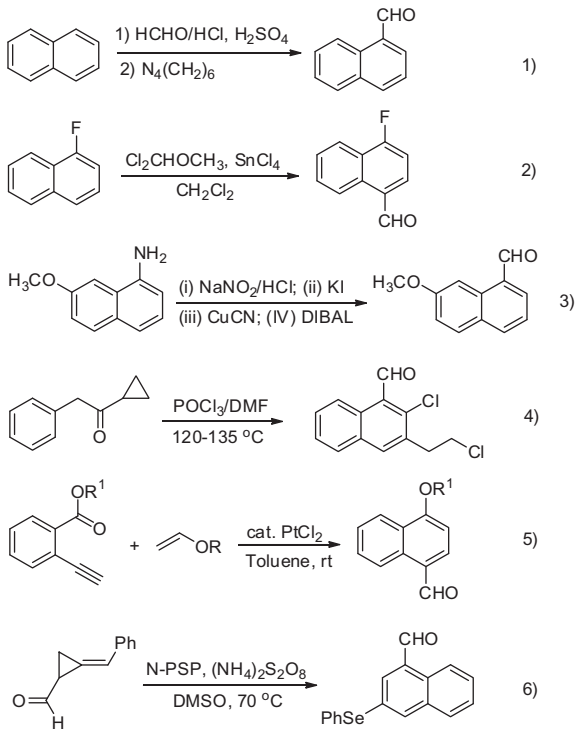
Introduction

Aldehydes are undoubtedly one of the most important classes of organic compounds as their diverse reactivity has made them indispensable as synthetic intermediates in the preparation of a myriad of functional organic molecules.[1] Among them, 1-naphthaldehyde and its derivatives have found wide applications in the synthesis of different kinds of pharmaceuticals and fine chemicals.[2] Due to their importance, a number of methods to prepare 1-naphthaldehydes have been developed. One of the most frequently used strategies involves the regio-selective introduction of the formyl group onto the existing naphthalene scaffold or via the transformation of other functional groups into the aldehyde. As an example, α-naphthaldehyde was synthesized by treating α-chloromethylnaphthalene with hexamethylenetetramine, and the required α-chloromethylnaphthalene was obtained by reacting naphthalene with formaldehyde and hydrochloric acid followed by treatment with concentrated sulfuric acid (Scheme 1, 1).[3] In another example, Boswell, et al reported that 4-fluoro-1-naphthaldehyde could be obtained with good yields by formylation of 1-fluoronaphthalene with dichloro methyl methyl ether and tin (IV) chloride (Scheme 1, 2).[4] The third example involves the preparation of 7-methoxy-1-naphthaldehyde from the corresponding amine (Scheme 1, 3).[5] Thus, diazotization of 7-methoxynaphthalen-1-amine followed by treatment with potassium iodide gave 1-naphthyl iodide. Cyanation with an excess amount of copper(I) cyanide followed by reduction with DIBAL afforded 7-methoxy-1-naphthaldehyde. As the second strategy, 1-naphthaldehydes were prepared via the annulation reactions of functionalized benzenes. In this regard, Shi reported a convenient method to synthesize 2-chloro-3-(2-chloroethyl)-1-naphthaldehydes via the Vilsmeier–Haack reaction of 1-cyclopropyl-2-arylethan- ones (Scheme 1, 4).[6] More recently, Iwasawa reported a concise method for the preparation of 4-alkoxy or 4-alkyl sulfanyl-1-naphthaldehydes by reacting *o*-ethynylbenzoates or benzothioates with vinyl ethers in the presence of $PtCl_2$ (Scheme 1, 5).[7] In addition, 1-naphthaldehydes have also been prepared through the intramolecular alkylation and cyclization of (*E*)-2-(arylmethylene)cyclopropylaldehyde mediated by organo-selenium reagents (Scheme 1, 6).[8] While these literature protocols are generally efficient and reliable, some of them more or less still suffer from tedious operation procedures, harsh reaction conditions, and toxic or expensive reagents. Therefore, to develop new synthetic methods to prepare 1-naphthaldehydes from readily available starting materials and under mild conditions remains an attractive but still challenging task.

As a continuation of our recent interests in exploring the versatile reaction patterns of allenic alcohols and homo-propargyl alcohols,[9] and inspired by the diverse reactivity of iodine monochloride (ICl) demonstrated in various transformations,[10] we have studied the reaction of 1-phenylpent-4-yn-2-ols in the presence of ICl. From this reaction, a convenient and efficient synthetic approach toward 1-naphthaldehydes was successfully developed. Herein, we report our results in this aspect.

* Corresponding author. Tel.: +86 373 3329261; fax: +86 373 3329275.
E-mail address: xuesen.fan@htu.cn (X. Fan).

http://dx.doi.org/10.1016/j.tetlet.2016.03.047
0040-4039/

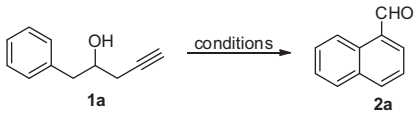


Scheme 1. Literature methods for the preparation of 1-naphthaldehydes.

Initially, 1-phenylpent-4-yn-2-ol (**1a**) was treated with 1 equiv of ICl in CH_2Cl_2 at ambient temperature for 0.5 h. From this reaction, to our delight, 1-naphthaldehyde (**2a**) was obtained in a yield of 38% (Table 1, entry 1). To improve the efficiency, different solvents including CH_3CN, CH_3OH, DMF and THF were then tried. However, they were found to be much less effective than CH_2Cl_2 in mediating this reaction (entries 2–5). When the amount of ICl was reduced to 0.5 equiv, the yield of **2a** decreased obviously (entry 6). On the other hand, the yield of **2a** could be increased to 64% when 2 equiv of ICl were used (entry 7). Further an increase in the amount of ICl did not result in higher yields of **2a** (entries 8–9). In the following studies, the reaction of **1a** was tried at temperatures lower or higher than room temperature (entries 10–11). However, no improvement in the yield of **2a** was observed. Finally, $FeCl_3$, BBr_3, and I_2 were also tried as possible reagents to replace ICl to promote this transformation (entries 12–14). Unfortunately, no desired product was obtained from these reactions.

With the optimized reaction conditions in hand, the scope and generality of this novel synthesis of 1-naphthaldehydes was studied. Thus, several 1-phenylpent-4-yn-2-ol substrates (**1**) with different substituents on the phenyl ring were prepared and treated with ICl.[11] The results listed in Table 2 showed that while the R

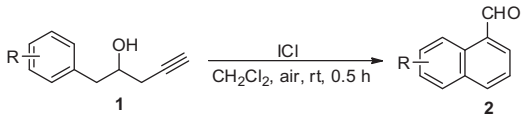
Table 1
Optimization study on the synthesis of **2a** from **1a**[a]

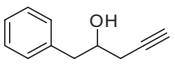
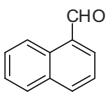
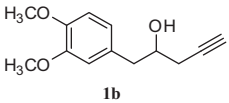
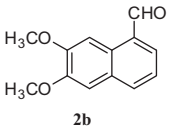
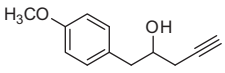
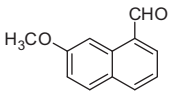
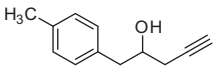
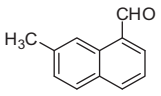
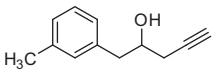
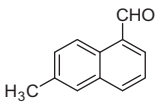
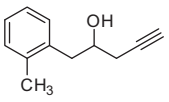
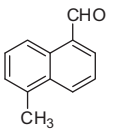
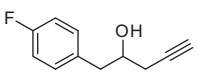
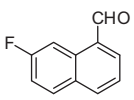
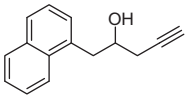
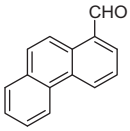


Entry	Promoter (equiv)	Solvent	*T* (°C)	Yield[b] (%)
1	ICl (1)	CH_2Cl_2	rt	38
2	ICl (1)	CH_3CN	rt	8
3	ICl (1)	CH_3OH	rt	—
4	ICl (1)	DMF	rt	—
5	ICl (1)	THF	rt	7
6	ICl (0.5)	CH_2Cl_2	rt	27
7	ICl (2)	CH_2Cl_2	rt	64
8	ICl (3)	CH_2Cl_2	rt	65
9	ICl (4)	CH_2Cl_2	rt	60
10	ICl (2)	CH_2Cl_2	0	23
11	ICl (2)	CH_2Cl_2	40	62
12	$FeCl_3$ (2)	CH_2Cl_2	rt	—
13	BBr_3 (2)	CH_2Cl_2	rt	—
14	I_2 (2)	CH_2Cl_2	rt	—

[a] Reaction conditions: 0.5 mmol of **1a**, solvent (2 mL), ICl (1 M in CH_2Cl_2), air, 0.5 h.
[b] Isolated yield.

Table 2
Substrate scope for the synthesis of **2**[a]



Entry	Substrates	Products	Yield[b] (%)
1	 **1a**	 **2a**	64
2	 **1b**	 **2b**	73
3	 **1c**	 **2c**	71
4	 **1d**	 **2d**	68
5	 **1e**	 **2e**	71
6	 **1f**	 **2f**	65
7	 **1g**	 **2g**	55
8	 **1h**	 **2h**	67

[a] Reaction conditions: 0.5 mmol of **1**, CH_2Cl_2 (2 mL), ICl (1 mL, 1 M in CH_2Cl_2), air, rt, 0.5 h.
[b] Isolated yield.