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One-pot synthesis of acenaphtho[1,2-*b*]furan derivatives

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Abstract

New 9-(alkyl or aryl)acenaphtho[1,2-*b*]furan-8-(alky or aryl)amine compounds has herein been reported by one-pot reaction of (acenaphthylen-1-yloxy)trimethylsilane, alkyl and aryl aldehydes, and aryl and alky isocyanides in refluxing DMF.

Keywords: One-pot reaction; Acenaphtho[1,2-*b*]furan-8-amine; Isocyanides

Modern industry prefers synthetic approaches with minimum steps along with maximum complexity of product [1]. A multi-component reaction (MCRs), which makes possible combinatorial reactions between simple starting materials and producing target product in one-pot operation, is one of the best approaches to fulfill this aim. MCRs have been associated with advantages, such as simplified purification due to incorporation of all starting material into the final product, not producing by product, minimizing reaction steps and producing structurally divers products from starting materials, which all of them are pronounced advantages over traditional synthetic approaches [2–7].

Designing synthetic plans for Fused furan heteroaromatic compounds [8,9], which abundantly occur in nature, have recently gained considerable attention because of their pharmacologically and biologically activities and also because of their applications as efficient intermediate in preparation of other natural products [10,11]. Although various synthetic approach have ever been introduced for fused furans, isocyanide based MCRs emerged 1990s by Passerini [12] have predominated because of simplified performance, easy purification and capability of producing structurally divers furans in one-pot operation [13–19]. To the best our knowledge, there are no published reports which are devoted to the synthesis of acenaphtho[1,2-*b*]furan derivatives. With these considerations in mind, we designed a one-pot synthesis for the preparation of the 9-substituted acenaphtho[1,2-*b*]furan-8-amine derivatives **7a**–**r** starting from (acenaphthylen-1-yloxy)trimethylsilane, alkyl and aryl aldehydes and aryl (or alkyl) isocyanides (Table 1).

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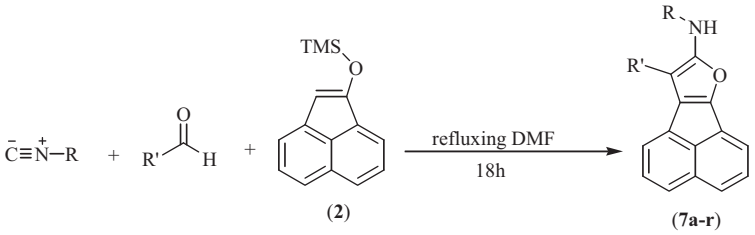
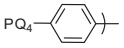
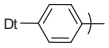
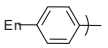
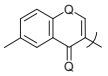
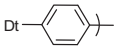
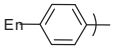
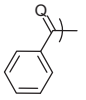
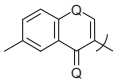
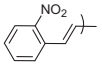
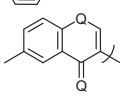
Table 1
One-pot three-component synthesis of compounds **7a–r**. .



Entry	R	R′	Product	Yield (%)[a]	Entry	R	R′	Product	Yield (%)[a]
1			**7a**	82	10			**7j**	72
2			**7b**	86	11			**7k**	87
3			**7c**	79	12			**7l**	84
4			**7d**	84	13			**7m**	82
5			**7e**	81	14			**7n**	93
6		H	**7f**	88	15			**7o**	74
7			**7g**	83	16			**7p**	70
8			**7h**	75	17			**7q**	75
9		Propyl	**7i**	82	18			**7r**	73

[a] Refers to purified yield.

1. Results and discussions

Teimouri and Mansouri in 2008s [20] reported catalyst-free synthesis of phenaleno[1,2-*b*]furan derivatives starting from aryl and alky aldehydes, alkyl and aryl isocyanides, and 2*H*-phenalene-1,3-dione in one-pot operation. Knoevenagel intermediate resulting from condensation of isocyanide-activated 2*H*-phenalene-1,3-dione with aldehyde have been established as typical intermediate in this kind of reaction. Accordingly, we envisioned to apply the same synthetic approach into the preparation of 9-substituted acenaphtho[1,2-*b*]furan-8-amine using acenaphthylen-1(2*H*)-one, benzaldehyde and isocyanocyclohexane as starting components (Fig. 1). Although, experimental attempts on the preparation of these compounds were failed, and monitoring the reaction by TLC showed that the starting substrates had remained unchanged even after 36 h as well as even at the presence of DABCO which is a typical base in this type of reactions [11] It is presumable two hydrogens on the adjacent carbon to the carbonyl group of acenaphthylen-1(2*H*)-one are not enough acidic to form corresponding enolate at the presence of relatively weak

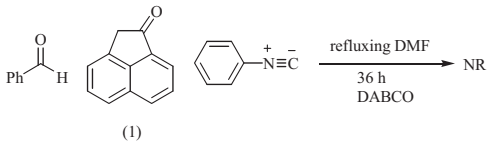


Fig. 1. Unsuccessful attempt on the preparation of aminofuran.

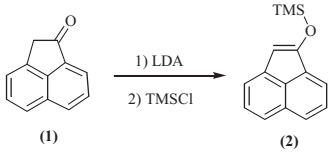


Fig. 2. Preparation of (acenaphthylen-1-yloxy)trimethylsilane (**2**) from acenaphthylen-1(2*H*)-one (**1**).

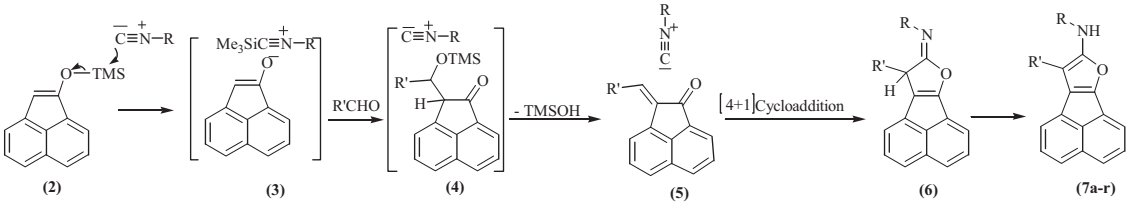


Fig. 3. Proposed mechanism for one-pot three-component synthesis of compounds **7a**–**r**.

bases such as isocyanocyclohexane or DABCO. To get round the problem, we converted acenaphthylen-1(2*H*)-one to the corresponding silyl enol ether (Fig. 2) which afforded desired product (**7g**) in 83% yield when was refluxed along with benzaldehyde and 1-isocyanobenzene for 10 h in DMF (Table 1, entry 7).

Effect of temperature was evaluated by carrying out the reaction at the various temperatures. The chemical yields increased as reaction temperature was raised. Hence, refluxing temperature was chose as optimum temperature and applied for all the reactions. Various solvents such as CH_2Cl_2, $CHCl_3$, ethanol, CH_3CN and toluene were screened for the reaction and DMF was found out as the best choice.

To disclose generality and scope of the reaction with respect to aldehyde, we examined various aliphatic aldehydes, such as α,β-unsaturated aldehydes and substituted aromatic aldehydes containing electron-withdrawing and electron-releasing substituent groups, and it was disclosed that all of them were capable of tolerating reaction conditions with good yields (Table 1, entries 1–12). In addition, we investigated limitations and scope of the reaction with respect to isocyanide component. We applied aliphatic and aromatic isocyanides, and found out that the reaction efficiently proceeded even with hindered aliphatic and aromatic isocyanides (Table 1).

We have postulated a mechanism for these reactions which is in agreement with well-known mechanisms which have recently been reported (Fig. 3) [11,20].

The first step presumably involves nucleophilic attack of isocyanide on silyl enol ether (**2**), resulting in disconnection of O-$SiMe_3$ linkage and generation of an active enolate which is present as counter anion in ion pair complex (**3**). Aldol adduct (**4**), which is formed from nucleophilic attack of generated enol on aldehyde, can lose a molecule of $(CH_3)_3SiOH$ to afford α,β-unsaturated keton (**5**). This is probably followed by [4 + 1] cycloaddition reaction to give iminolactone intermediate (**6**). Benefiting from delocalization stability, iminolactone (**6**) is driven to undergo isomerization to full conjugated aminofuran heteroaromatic moiety (**7**).

2. Experimental

All products are new and were characterized by IR, ^{1}HNMR, ^{13}CNMR and elemental micro analyzing. ^{1}HNMR spectra were recorded on a Bruker AQSAVANCE-400 MHz spectrometer using TMS as an internal standard ($CDCl_3$ solution). ^{13}CNMR spectra were recorded on a Bruker AQSAVANCE-125 MHz spectrometer ($CDCl_3$ solution). IR

spectra were recorded from KBr disk on the FT-IR Bruker Tensor. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Thin layer chromatography (TLC) on commercial aluminum-backed plates of silica gel, 60 F254 was used to monitor the progress of reactions. (Acenaphthylen-1-yloxy)trimethylsilane (**2**) was prepared according to the literature [21].

*2.1. General procedure for preparation of acenaphtho[1,2-b]furan derivatives **7a–r***

To a magnetically stirred mixture of aldehyde (1.0 mmol) and (acenaphthylen-1-yloxy)trimethylsilane (**2**) in DMF (40 mL) was dropwisely added a solution of isocyanide (1.0 mmol) in DMF (10 mL) over a 15 min-period at −78 °C. Subsequently, the reaction was slowly allowed to warm to room temperature and then refluxed for 18 h. Then, the reaction mixture was cooled and washed with water (3×20 mL) and extracted with CH_2Cl_2 (4×15 mL). Evaporation of volatile form organic layer left a solid which was washed with Et_2O and stored as final product.

References

[1] B.M. Trost, Science 254 (1991) 1471.
[2] Y. Dai, B.D. Li, et al. Chin. Chem. Lett. 21 (2010) 31.
[3] Y.B. Jiang, C.X. Kuang, Chin. Chem. Lett. 20 (2009) 545.
[4] Y. Liang, L.M. Tang, et al. Chin. Chem. Lett. 21 (2010) 991.
[5] Y. Yang, H.G. Hu, et al. Chin. Chem. Lett. 20 (2009) 52.
[6] R. Sandaroo, S. Damavandi, A. Nazif, et al. Chin. Chem. Lett. 22 (2011) 213.
[7] A. Kuraitheerthakumaran, S. Pazhamalai, M. Gopalakrishnan, Chin. Chem. Lett. 22 (2011) 1199.
[8] F.M. Dean, Adv. Heterocycl. Chem. 30 (1982) 167.
[9] B.H. Lipshutz, Chem. Rev. (1986) 795.
[10] D.D. Sternbach, D.M. Rossana, Tetrahedron Lett. 23 (1982) 303.
[11] B. Baghernejad, M.M. Heravi, H.A. Oskooie, et al. Mol. Divers. 15 (2011) 245.
[12] M. Passerini, Gazz. Chim. Ital. 52 (1922) 432.
[13] V. Nair, R.S. Menon, A.U. Vinod, S. Viji, Tetrahedron Lett. 43 (2002) 2293.
[14] A. Shaabani, M.B. Teimouri, H.R. Bijanzadeh, Tetrahedron Lett. 43 (2002) 9151.
[15] A. Shaabani, M.B. Teimouri, H.R. Bijanzadeh, Monatsh. Chem. 135 (2004) 441.
[16] A. Shaabani, M.B. Teimouri, H.R. Bijanzadeh, Monatsh. Chem. 135 (2004) 589.
[17] A. Shaabani, M.B. Teimouri, S. Samadi, K. Soleimani, Synth. Commun. 35 (2005) 535.
[18] M.B. Teimouri, R. Bazhrang, Bioorg. Med. Chem. Lett. 16 (2006) 3697.
[19] M.B. Teimouri, H.R. Khavasi, Tetrahedron 63 (2007) 10269.
[20] M.B. Teimouri, F. Mansouri, J. Comb. Chem. 10 (2008) 507.
[21] J.J. Song, Z. Tan, J.T. Reeves, et al. Org. Lett. 10 (2008) 877.